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EXPERIMENTAL CHEMISTRY.

J.

EXPERIMENTAL CHEMISTRY

FOR

JUNIOR STUDENTS

BY

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CHAP. I. TO XVI.

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PREFACE

TO

THE SECOND EDITION.

THE necessity for the issue of a Second Edition of Parts I. and II. has given me the opportunity to make a few verbal corrections, and some additions required by our advancing knowledge. Otherwise the work retains the form in which I am glad to know it has proved acceptable to teachers and students.

November, 1882.

J. E. R.

PREFACE

TO

THE FIRST EDITION.

THIS work is identical in plan with my *Six Lectures on Experimental Chemistry*, but different in style, and much extended in range, so as to include the amount of knowledge of fact and principle usually expected from junior Arts, Medical and Pharmaceutical Students, as well as from the higher classes in Intermediate Schools.

The system pursued in this book is designed to lead the student through a series of connected experiments—often *quantitative* in form—and to assist him in the interpretation of his results, and in devising modes of testing the validity of the conclusions drawn from them. Thus while acquiring a tolerably wide knowledge of fact, the student receives a certain amount of training in the purely 'experimental method' of investigating Nature. If this training be sound, the study of Chemistry must prove a valuable means of mental education. How far the particular plan pursued in the following pages is likely to contribute to such a result, I must leave others to judge :

but a reviewer of my *Lectures* was so good as to say :—' In these Lectures the author departs widely from the usual routine of elementary treatises. . . . We believe that he is right in the plan he has adopted, and that instruction of this nature would greatly facilitate the acquisition of clear and distinct ideas of the leading facts and laws of Chemistry.' (*Chemical News*, vol. xxix. page 227.) This work is divided into four parts, each one being, as far as practicable, complete in itself. Part I. is introductory, and deals with first principles, and with the chemistry of the typical elements, hydrogen and oxygen, and their compounds ; Part II., with the rest of the non-metals ; Part III., with the metals ; and Part IV., with organic chemistry. The experiments described are, whenever possible, those easily performed ; in some cases, however, methods are necessarily detailed which the student may not have either the skill or the means to carry out, but he should endeavour to see these operations carefully conducted. It is assumed throughout that the reader can obtain some practical instruction in glass working and the construction of apparatus.

It is only necessary to add that the complete work will contain the solutions of all the problems in my *Lecture Note Book.*

<div align="right">J. E. R.</div>

CHEMICAL LABORATORY,
TRINITY COLLEGE, DUBLIN :
November, 1880.

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INTRODUCTION

TO

EXPERIMENTAL CHEMISTRY.

PART I.

CHAPTER I.

PRELIMINARY EXPERIMENTS.

CHEMISTRY has for its object the discovery of the laws which govern the *composition* of all material things, and the action of one kind of matter upon another in all cases involving change in composition. This knowledge is acquired by experiment, accurate observation of the phenomena presented during an experiment, and careful reasoning upon the result. The following pages contain numerous illustrations of the application of this experimental method of inquiry in the study of chemistry.

Experiment 1.—Let us commence our course with a simple experiment.

Hold by means of a small pincers or tongs a piece of thin wire of the metal platinum in the flame of a

spirit lamp, as in fig. 1, or in that of a Bunsen gas-burner. Observe that the wire soon becomes red-hot and glows as long as it is held in the flame; but, when removed and allowed to cool, it resumes its

FIG. 1.
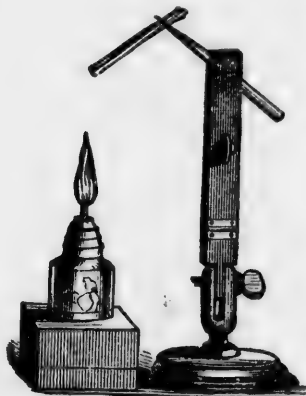
original appearance, and if weighed before and after the experiment, no difference is observed. Therefore the change from cold to red-hot platinum is but a *temporary* one, the metal remaining unchanged in form and substance.

Experiment 2. — Now make an identical experiment with a piece of magnesium wire or ribbon. Observe that the metal soon begins to burn and emits much light, even when removed from the source of heat. It also gives out white fumes and leaves a white substance behind which, though retaining some of the form of the original wire or ribbon, can be easily powdered when cold, and is seen to be utterly unlike the metal which produced it. Moreover, the white substance is found to *weigh more* than the magnesium originally taken. In this case, a change has taken place on heating, and it is *permanent*.

The temporary alteration of the platinum wire is not accompanied by any difference in composition, and is spoken of as a *physical* change; that of the magnesium, as a *chemical change*, and the action, as

chemical action, because a material alteration in composition has taken place, as shown by the gain in weight; and a new body has been produced, evidently possessing characters which serve to distinguish it completely from the metal magnesium, and, indeed, from all other known substances.

All observed changes in matter can be placed in one or other of the above classes, but it is with chemical change and chemical action that we are principally concerned.

In the experiment with magnesium it was shown that the application of *heat* served to bring about chemical change, but we shall find as we proceed that chemical action can be determined by other agents—namely, by *Mechanical force, Light, Electricity,* and a peculiar force called *Chemical attraction,* or 'affinity,' which acts only at excessively minute distances.

Experiment 3.—Place two or three small crystals (not more) of the salt called potassium chlorate in a stone-ware mortar, powder the substance and add half as much sulphur, also in powder. Mix gently and then give the mixture a sharp blow with the pestle. A report follows, indicating that chemical action has taken place, in this instance determined by *mechanical force.*

Experiment 4.—Again, dissolve a few crystals of silver nitrate in half a test tube of water and paint the liquid over some ordinary writing paper in a darkened room. Then divide the paper into two parts: preserve one in a drawer, and immediately expose the other to full sunlight or diffused daylight. The exposed paper will shortly discolour and assume

a chocolate brown tint, or even a bronzy black colour --the result of chemical change brought about by the agency of *sunlight*, for the paper preserved from light does not suffer any apparent change in the same time. The art of photography depends upon similar changes brought about by light.

Experiment 5. Now take the little galvanic cell described at page 6 (see fig. 2, A) and attach a small slip of sheet platinum to the end of the wire from *Zn*,

Fig. 2.

Zn — Cu

A   B
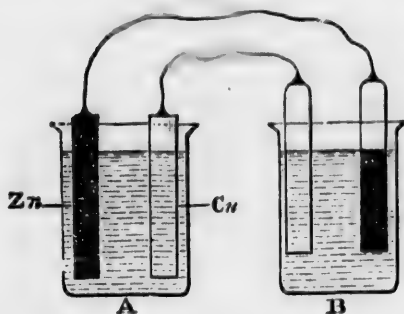
and connect a slip of copper with *Cu*; dip both in a strong solution of copper sulphate contained in B. Remove the slips after a few minutes and observe that a reddish deposit has formed on the slip connected by wire with the zinc plate *Zn*, of the cell. If the action be continued for some hours, a considerable layer of red metallic copper is obtained on the slip as the result of chemical change determined by *electricity* in the solution of copper sulphate. The art of electro-typing depends on this power exerted by electricity.

Experiment 6.—Finally, if we add to a small globule of the liquid metal mercury, or quick-silver, contained in a mortar, a few fragments of iodine, and mix them together with the pestle, the metal and iodine gradually disappear and a powder is formed. If the proportion of iodine used be large,

the resulting powder is red in colour; if little iodine be employed, the colour is a dull green. Here the two bodies named produce a new substance when brought near to each other, and this change is alone due to the *chemical attraction* of one body for the other. The exercise of this attractive force is facilitated by the liquidity of the metal, and the change is hastened by the addition of a few drops of spirit of wine, which dissolves some of the iodine and thus enables the particles of the latter to move more freely. This chemical attraction differs from other forces in the important particular that it only acts at excessively minute distances. This may be further illustrated in the following way :—

Experiment 7.—Mix in any dry glass vessel, such as a beaker or a tumbler, a tea-spoonful of 'bread soda,' or sodium bicarbonate, and the same quantity of finely powdered tartaric acid.[1] However closely the solid particles are brought together by stirring or rubbing, no action takes place, provided the mixture is dry. Add now some water to the powder, and violent effervescence ensues, indicative of chemical action. Water added to the acid or the soda *separately* does not cause any effervescence and merely dissolves each body, the violent action observed on addition of water to the mixed powders must therefore have been due to the mutual attraction of the two solids leading to chemical action ; but that action could only take place when, by solution in water, the particles of each body were endued with greater mobility than in the

[1] Or the contents of the two papers sold as 'Seidlitz powder' may be mixed instead of the above.

solid state, and were thus enabled to get within the sphere of each other's attraction.

We thus learn that chemical action is greatly facilitated by the solution or liquidity of one or all of the bodies engaged. We shall find later on, Experiment 53, that a fine state of division of a solid tends to a similar result.

In some of the experiments already cited, the student will have observed the evolution of *heat* and *light* during chemical action. Thus, when the magnesium wire burned in air, much heat and an intense light were produced. But *electricity* is also freely developed in certain chemical actions, and in fact the source of electricity in an ordinary galvanic cell is chemical action.

Experiment 8.—The simplest form of galvanic cell may be easily made thus:—Take a glass vessel, such as a tumbler (A, fig. 3), and fill it about two-thirds with water, to which one-tenth part of oil of vitriol (sulphuric acid) has been added. Next cut a slip of clean sheet zinc, Zn, a little longer than the glass; its width may be equal to half the diameter of the vessel. Make a hole through one end of the slip, pass a piece of bright copper wire through it and fasten securely by twisting the wire. Prepare
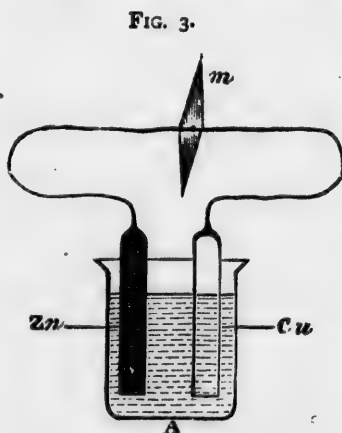
FIG. 3.

a similar slip of clean copper, *Cu*, with its wire, and the apparatus is complete. When the two wires are connected, as shown, and the plates immersed in the liquid, *without touching one another*, the zinc alone dissolves in the acid, the copper not being chemically acted on, while a current of electricity flows along the wire, and may be easily detected by bringing the wire over and parallel to the magnetised needle, *m*, of a toy compass. The needle tends to set itself at right angles to the wire, but if the chemical action be stopped, by taking the plates out of the liquid, and the connecting wire be brought over the needle as before, no motion takes place, as the wire no longer conveys electricity. The compass needle, therefore, serves as a detecter of electric currents circulating through copper wires.

When two or more of such simple galvanic cells as that just described are joined, usually in such a way that the zinc plate of one cell is coupled with the copper plate of the next, a *galvanic battery* of the simplest kind is obtained; but for details concerning galvanic cells and batteries, a work on Physics must be consulted.

Again turning to the experiment with burning magnesium, we find that it is capable of affording us another item of information. We pointed out that the white substance produced when the metal burns weighed *more* than the magnesium originally taken. In this case, then, heat enabled the magnesium to take to itself some other body which could only be derived from the air in which the metal was heated. The chemical action thus induced by heat was one of

combination, or the union of unlike kinds of matter.

Experiment 9.—The same agent—heat—is capable of effecting the reverse change. If we take a small quantity of the well-known white, crystalline and transparent substance called *silver nitrate,* and heat it gently in a small dry test tube, the body is seen to melt to a yellowish liquid, and, on continuing the heat, bubbles rise through the liquid and ruddy fumes pour out of the mouth of the tube. If we continue to heat until all action is over, and break the tube when cold, the residue is seen to consist of pure white metallic silver. In this case the chemical action brought about by heat resulted in *decomposition,* or resolution, of the silver nitrate into the metal silver, and some other kind of matter seen to be driven off as coloured vapour or gas.

Since chemical action may result either in *combination* or *decomposition,* it follows that chemical substances may be conveniently divided into two great groups: first, those forms of matter which do not suffer decomposition by the exercise of any force at our command; and, secondly, those bodies capable of resolution into some two or more members of the first group. The forms of matter included in the first group are called *elements,* and those in the second, *compounds.* The decomposition of a compound into its elements is spoken of as a process of *analysis,* and the production of a chemical compound from its elements is termed *synthesis.*

The researches of chemists up to the present time have made known to us some sixty-six elements. The

names of the most important of these are given in the table, which will be found at page 64. But it is necessary to guard carefully against the idea that the 'elements' so-called are certainly simple bodies: we cannot at present prove them to be compounds—that is all we can say.

All known chemical compounds are the result of union between some two or more elements; but the important question now arises whether this union is in the nature of a mere mixture, or of something much more intimate.

Experiment 10.—Make a mixture of iron filings with about two-thirds of their weight of sulphur (the 'flour of sulphur' of the druggists). A greenish-grey powder results, but distinct particles of iron and of sulphur can be easily recognised in it, not only with the aid of a magnifying glass, but also by stirring some of the powder into a considerable quantity of water, when the heavy particles of iron fall quickly to the bottom of the vessel, while the lighter sulphur more slowly subsides and collects as a distinct layer. Or the iron can be still more easily separated from the sulphur by means of a small horse-shoe magnet. If the latter be passed through some of the powder, the particles of iron are attracted by the poles of the magnet, and attach themselves so firmly that the particles of sulphur—which are not attracted but mechanically adherent—may be blown away, leaving the metallic iron behind.

The constituents of this mixture can therefore be separated by mechanical means. Moreover, its properties partake of those of iron and sulphur.

Experiment 11.—Now heat *very strongly* a portion of the original mixture in a tube of Bohemian or hard glass ; [1] note that the mixture becomes pasty and then glows for a short time. Cool and remove the resulting dark substance from the tube. When examined with a magnifying glass, no particles of iron or sulphur can be detected, if the mixture was sufficiently heated ; moreover, it is not attracted, or but slightly, by the magnet, and therefore does not any longer contain *free* metallic iron. The iron and sulphur are no longer separable by mechanical means, and the properties of the body resulting from the fusion do not partake of those of free iron or free sulphur. In fact, the glowing observed on heating the mixture was due to chemical combination between the two elements, and the product of that union—a body termed iron sulphide—possesses a definite group of characters which not only serve to distinguish it from the free elements iron and sulphur, or a mixture of them, but from all other known bodies.

Experiment 12.—Mix twelve parts by weight of finely-powdered charcoal (a form of the element *carbon*) with sixty-four parts of sulphur, also in a fine state of division. The mixture is an opaque, almost inodorous, dull, yellowish powder that may be exposed to the air for an indefinite time without loss of weight or other alteration. Now obtain a specimen of the liquid termed ‘carbon bisulphide,’ which is a chemical compound of carbon and sulphur *in exactly the same propor-*

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[1] A glass which fuses with great difficulty, and hence may be suitably used in operations requiring a temperature so high as to easily melt ordinary glass tubing.

tions as the mixture of the two elements already made. This liquid [1] is perfectly transparent and colourless, and has a most disagreeable smell, while it is so volatile that a few drops let fall upon a plate disappear in a very short time. We thus learn still more clearly that a wide difference in properties may exist between a definite chemical compound and a mere mechanical mixture of its constituents. The special properties of the elements can be easily recognised in the mixture, but not in the definite chemical compound, unless we decompose the latter and sever the union of its components.

Thus in effecting the synthesis of a new chemical compound from its elements, the philosophic chemist performs an operation which approaches more nearly than any other to a *creative act.*

[1] For the preparation of this body see Part II. page 342. It must be handled with care, as it is very inflammable.

CHAPTER II.

EXPERIMENTS WITH SILVER NITRATE AND MAGNESIUM.

A KNOWLEDGE of the chief Laws of Chemistry can be more simply and naturally attained by the study of chemical *compounds* in the first instance than by the detailed examination of simple bodies or elements,

FIG. 4.
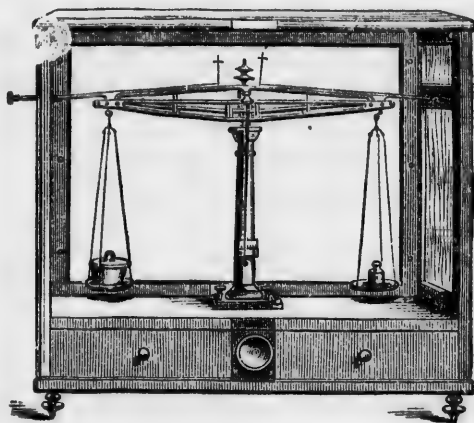
and the most easily managed compound with which the beginner can experiment is the SILVER NITRATE.

It has been already proved by Experiment 9 that Silver Nitrate is resolved into metallic silver and coloured gas, when strongly heated in a glass tube.

Let us now examine this case of *decomposition* with the aid of a balance or delicate scales, one of the best forms of which valuable instrument is represented in fig. 4.[1]

Experiment 13.—Break up in a perfectly clean mortar some clear and pure *crystals* of silver nitrate ;[2] then press the powder between folds of white blotting-paper, in order to remove any trace of moisture. Next take a stout test tube of *hard* glass, measuring 12 centimeters long and 12 millimeters in diameter ; take care that it is clean and dry; then place it on one pan of the balance and counterpoise by placing a small pill box on the other pan, and adding grains of shot or pieces of tinfoil until equilibrium is established. Next place in the pan, along with the shot or foil, weights representing 170 centigrams (=1·7 grams), and now pour into the test tube on the other pan the powdered silver nitrate until the weights are balanced. The test tube then contains 170 centigrams of the silver compound. Now support the tube in a slanting position in the wooden clip shown in fig. 1, and gently heat the bottom of the tube with a spirit lamp, or a Bunsen gas-burner of the form shown in fig. 5. The silver nitrate melts quietly to a

[1] Much cheaper balances than that figured can now be obtained, which will indicate less than 1 milligram when loaded with 25 grams. When the student cannot obtain the use of a balance, he should perform the experiments as described without weighing the materials or products.

[2] The crystals are alone certain to give satisfactory results, as the ' Lunar Caustic,' sold in sticks, is sometimes adulterated and often impure.

clear liquid. If the temperature be now increased by bringing the flame closer, slight effervescence is observed—due to the escape of bubbles of gas. Soon reddish brown fumes appear, and these pass away into the atmosphere, while the residue in the tube loses much of its transparency owing to evident deposition of solid matter. The heating must be continued in such a way as to prevent any loss by spirting solid particles out of the tube, and until the ruddy fumes are completely dissipated and pure silver alone remains; finally, let the flame play on the sides of the tube so as to ensure the decomposition of any particles of the nitrate that may have yet escaped the full action of the heat.[1] When cold, replace the tube on the pan of the balance and adjust the weights in the other pan so as to restore equilibrium; the weights required represent the pure silver thus obtained from 170 centigrams of silver nitrate.

Two separate experiments made in the way described afforded the following results :—

Weight of metallic silver obtained from 170 centigrams of pure silver nitrate.

1st experiment	.	108·22 c. grs.
2nd „	.	108·40 c. grs.

The second experiment was made by a young student but little skilled in chemical manipulation.

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[1] The *ultimate* decomposition may be thus represented :—

$$Ag\ NO_3 = Ag + NO_2 + O.$$

Now, it is found that the more carefully the experiment is made, the nearer does the result approach to 108; we may therefore say that 170 c. grs. of pure silver nitrate contain 108 c. grs. of the metallic element silver. Whatever may be the source of the silver nitrate taken, provided it be pure, and whatever the quantity employed in the experiment, provided the decomposition be carefully conducted, the weight of metal left after heating is always in the ratio of 108 to 170 of the silver nitrate employed. Thus we learn,

1st. That pure silver nitrate is a compound body.

2nd. That 170 parts of it contain 108 of pure elemental silver.

3rd. That it is *constant in composition.*

These are facts : the inference clearly to be drawn from them is that chemical compounds are constant in composition. This inference is completely borne out by further experiments in the same direction, for it has been found that every chemical compound which possesses a group of characters serving to define it, and so to distinguish it from all other forms of matter, exhibits the remarkable constancy of composition just detected in the case of silver nitrate.

Upon this great principle, often termed the 'First Law of Chemistry,' the science really rests.

The admission of the constancy in composition of chemical compounds leads us to expect that chemical combination takes place in *definite proportions*, else it were impossible to obtain an adequate explanation of the fact that the constituents of such a compound as silver nitrate are always to be found in the body in fixed proportions. We can put this

inference to the test of experiment in the following way : —

Experiment 14.—Dissolve two or three medium crystals of silver nitrate in half a test tube of water, and throw in a small slip of magnesium ribbon. Now observe that the magnesium soon becomes coated with a dirty grey material which can be readily detached on shaking, and then falls quickly to the bottom of the tube. As the powdery substance is shaken off the slip, a fresh coating forms which can be again detached by shaking, leaving the magnesium thinner each time. This goes on until one of two things happens : either the magnesium slip disappears altogether, leaving the powdery deposit behind it if a relatively large quantity of silver nitrate [1] was taken in the first instance ; or, if the silver nitrate was used in a relatively small proportion, the magnesium slip no longer becomes coated and may be allowed to remain in the liquid without undergoing any further change.

We have next to examine the grey substance. Remove the magnesium slip, if any remains, and then pour off the clear liquid and drain it away from the

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[1] In this case the clear liquid should still contain some unchanged silver nitrate in solution. To test for this, add to some of the clear liquid, poured off into a test tube, a few drops of solution of common salt. If the fluid becomes milky and lets fall a white *precipitate*, silver is present. This *test* for silver depends upon the fact that silver easily unites with another element, chlorine, and forms therewith the insoluble body termed silver chloride, which separates out. Common salt contains the necessary chlorine, and thus acts as a *reagent* for silver. For an equation representing this change see page 143.

grey deposit as much as possible. Now take out some of the moist matter with a glass rod and place it on white blotting paper. If dried near a fire, the deposit becomes lighter in colour and appears as a fine powder, which, when rubbed with a polished knife blade, assumes a silvery lustre. By this means, and by chemical tests which will be described later on, this powder can be shown to consist of pure metallic *silver* in a very fine state of division. We conclude, then, that magnesium acts chemically on the silver nitrate in solution and decomposes it, precipitating metallic silver, while the metal magnesium disappears, evidently owing to solution in the liquid.

By a slight modification of the above experiment we can easily find the weight of pure silver deposited during the complete solution of a given weight of pure magnesium.

Experiment 15.—For this purpose, dissolve about 200 c. grs. (=2 grams) of pure silver nitrate (the precise quantity is immaterial) in about twenty cubic centimeters of distilled water contained in a perfectly clean porcelain crucible, which latter has been gently heated over the lamp flame to dry it, and then, when cool, counterpoised in the way already described in the experiment with the glass tube. Now take a piece of carefully cleaned and bright magnesium ribbon weighing about 10 centigrams—the exact weight must be accurately ascertained—and add it to the contents of the crucible, stirring the magnesium about occasionally with a short piece of glass rod, which latter must not be removed from the crucible until

the experiment ends. Silver separates as before, and after some time all traces of the magnesium disappear. The mixture is now allowed to stand for a short time, in order that all particles of the heavy silver may settle to the bottom, as much as possible of the clear liquid is then carefully poured away without disturbing the precipitate of silver. Some 20 or 30 cs. of distilled water are now to be added to the deposit, the latter well stirred up with the fresh water and then again allowed to stand, when the clear liquid may be decanted off as before without loss of silver. This process of 'washing by decantation' of the silver must be repeated five or six times in order to secure the complete removal of all soluble impurity from the metal. The crucible with its moist contents is next placed in a warm place to dry, and is then carefully heated over the spirit or gas lamp, as in fig. 5, for a few minutes, in order to ensure the removal of all traces of moisture. When cold, the crucible with the silver is replaced on the balance pan and the weight of the metal accurately ascertained.

FIG. 5.

An experiment performed as described afforded the following result :—10 centigrams of magnesium were added to 200 c. grs. of silver nitrate in solution, and the silver collected after the magnesium had wholly disappeared was found to weigh 88 c. grs.

By the following simple calculation we can find the weight of magnesium required to precipitate 108 c. grs. of silver from 170 c. grs. of the silver nitrate, in order to bring the statement of our result into harmony with that of our former quantitative experiment :—

$$88 : 108 :: 10 : 12.2$$

However frequently we repeat and vary the form of the above experiment, we find that for 108 c. grs. of pure silver, removed from a solution containing an excess of the nitrate, 12.2 c. grs. (or 12 c. grs., if the materials are absolutely pure) of metallic magnesium dissolve. In other words 12 c. grs. of magnesium exactly replace 108 c. grs. of silver contained, as we have already seen, in 170 c. grs. of silver nitrate. There is therefore no doubt that metallic magnesium and silver nitrate act upon one another, or interact, in *definite proportions.* All similar experiments have led to precisely the same result, hence the 'Second law of chemistry :'—

'*All chemical substances interact in definite proportions by weight.*'

The change on heating silver nitrate was one of *decomposition*, for 170 c. grs. of the compound broke up into 108 c. grs. of silver, and 62 c. grs. of the volatile matter we may provisionally group under the term ' nitrate;' but *combination* also, between the silver and the 'nitrate,' must have originally taken place in definite proportions.

Again, the change consequent upon the action of magnesium on silver nitrate was one of decomposition, and of combination, for while the silver nitrate was

decomposed and its silver separated just as completely as by heating the body alone, the 12 c. grs. of magnesium *combined* with the 62 c. grs. of 'nitrate,' and in fact the solution contained at the end of the experiment magnesium nitrate weighing 74 c. grs. (12+62 c. grs.), and that weight of the new compound thus formed could actually be separated from the liquid.

CHAPTER III.

EXPERIMENTS WITH MAGNESIUM AND HYDROGEN.

Experiment 16.—Half fill a test-tube with water to which two or three drops of oil of vitriol (sulphuric acid) have been added. Now plunge into the liquid a slip of magnesium ribbon and note the result. Brisk effervescence takes place, and the metal speedily disappears. The effervescence must be due to the escape of *gas*, and if we bring a flame to the mouth of the tube the gas takes fire and burns with slight explosions, but emits very little light while it burns.

Therefore magnesium, which displaces metallic silver from silver nitrate, causes the evolution of an inflammable gas from acidulated water. The next step is to collect some of this gas and examine its properties.

FIG. 6.

Experiment 17.—Take a glass tube closed at one end and about 20 centimeters long, and 2 centimeters in diameter, *t*, fig. 6; fill it completely with water acidulated with $\frac{1}{30}$th of its bulk of sulphuric acid ; then place a piece of cardboard, or better, a ground glass plate, over the mouth of the tube and
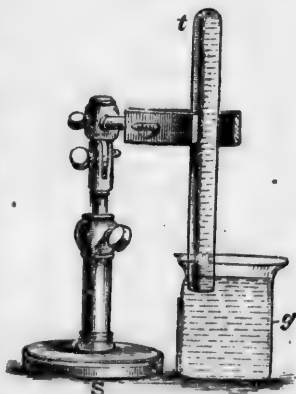
invert it. Next bring the mouth under the surface of a larger quantity of the acidulated water contained in the wide glass beaker, *g*, and support by means of the stand *s*.

So long as the mouth of the tube is under the surface of the liquid no air can enter, as the water is retained in the tube by atmospheric pressure. Now take a piece of magnesium ribbon about 20 centimeters long, crumple it up and rapidly pass it through the water and under the mouth of the inverted tube. It will ascend into the tube and cause effervescence as before, but the gas cannot escape into the air and therefore collects in the upper part of the tube, while it displaces a corresponding volume of water. As the magnesium dissolves add fresh pieces until the tube is filled with the gas.

Pass the plate under the water and close the mouth of the tube, then detach the latter from the stand, remove the tube, still closed with the plate, from the water, and examine the contents.

a. Note that the gas is free from colour.

b. Turn the mouth of the tube up quickly and apply it to the nose. No peculiar odour is perceived.

c. Refill [1] the tube with gas as before, and apply a

FIG. 6 *b.*
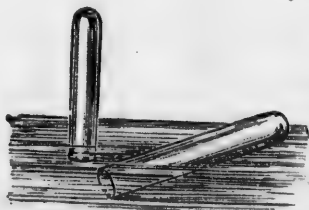
[1] Instead of refilling the large tube, the charge of gas collected in it in the first instance may be transferred to three small test tubes, if the latter are filled with water in a large dish or trough, inverted and held with the mouth of each under the surface of the liquid. The large tube of gas is carried to the water, and the mouth brought under one of the

flame to the mouth. The gas takes fire and burns with a pale blue flame.

d. Again fill the test tube with gas, turn the mouth of the tube *upwards* and remove the thumb. After a few seconds bring a flame to the mouth of the tube. No combustible gas is found in the tube.

We are, therefore, warranted in stating that the gas produced when metallic magnesium acts on acidulated water is colourless and inodorous. We may further assert that it cannot be soluble in water to any extent, as we are able to collect it easily over that liquid; indeed, it can be easily shown to be almost quite insoluble in water. It is combustible and is much lighter than atmospheric air, as evidenced by the rapidity with which it escapes on holding the tube with its mouth directed upwards. The gas possessing these properties chemists call HYDROGEN, and regard it as an elementary body.

Although hydrogen is an extremely light body—in fact, the lightest known form of matter—it admits of being weighed like all other material things, whether gases, liquids, or solids. Hence we can next set to work in order to answer the important question, What weight of hydrogen do 12·2 centigrams of magnesium displace from acidulated water?

Experiment 13.—With the aid of the apparatus shewn in fig. 7 an answer to this question can be easily obtained.

test tubes as shown, on inclining the large tube gas will pass from the latter up through the water and be caught in the test tube. Several tubes may thus be filled with gas from a single large vessel.

The flask A should be very light, and of about 50 cubic centimeters capacity; the little glass apparatus *a* should also be very light, and its tubes *c* and *d* must

FIG. 7
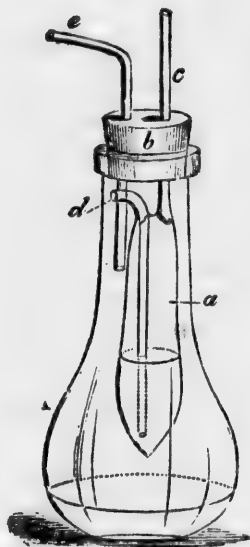
be fused into the glass. The tube *e*, like *c* and *d*, is open at both ends, but that within the apparatus need not project into the flask as shown in fig. 7, but may be cut off close to the cork.

In order to use the apparatus, fill the small inner flask *a* to the extent shown with strong oil of vitriol by removing the cork carrying the tubes and dipping *a* under some oil of vitriol, contained in a beaker, until the mouth of *d* is beneath the surface of the liquid. Suction applied at *c* causes the acid to enter to the desired extent, when the apparatus is removed from the acid, washed well externally with water so as to remove all acid from the exterior of *a* and from the mouth of the tube *d*. Before replacing the cork in A, drop into the latter exactly 12·2 centigrams of clean bright magnesium ribbon, along with the amount of water indicated in the sketch: then fix the cork in its place, plug the opening of *e* with a small piece of wax, dry the outside of the flask with a soft cloth, place it on one pan of the balance and accurately counterpoise the apparatus.[1]

[1] The apparatus, when ready for experiment, should not weigh more than 50 grams.

Next remove the flask to a sheet of clean white paper, slip a small piece of flexible tube over *c* and force air very gently into *a* until a few drops of oil of vitriol fall from *d* into the water in A containing the magnesium. Gas will soon be evolved, and this gas we already know to be hydrogen. It has no exit save through the tube *d*, and after bubbling through the oil of vitriol in *a* it escapes from *c* into the atmosphere. In its passage through the liquid the gas loses any moisture that it may carry with it, as the oil of vitriol possesses the convenient property of absorbing water with great avidity: hence only pure dry hydrogen, mixed at first with some air, escapes from *c*. As the evolution of gas slackens, a little more oil of vitriol can be forced over, and this operation repeated if necessary until the magnesium disappears. When this point is reached, remove the wax plug from *e* and place it on the balance pan, next apply suction to the flexible tube at *c*. Air is thus drawn in at *e* and replaces the last traces of the hydrogen thus sucked out and dried in its passage through *a*. The flask is wiped carefully, and replaced on the balance pan. It will now be found *lighter* than the counterpoise, indicating that it has lost matter during the experiment. The matter lost we know consists of the pure dry hydrogen gas, and the precise weight of it can be ascertained on restoring equilibrium by addition of weights to the pan on which the flask A rests.

When the experiment described is carefully conducted, 1 CENTIGRAM almost exactly restores equilibrium; therefore that is the weight of hydrogen

evolved during the solution of 12 centigrams of pure magnesium in acidulated water.

The results of the quantitative experiments hitherto performed may be stated thus, neglecting decimals :—

1	centigram	of HYDROGEN was separated by
12	c. grs.	,, pure MAGNESIUM, which also displaced
108	,,	,, pure SILVER from
170	,,	,, SILVER NITRATE.

The numbers so obtained are called *equivalents*, because they represent weights which are of *equal value* in chemical changes. In all such changes hitherto examined, hydrogen has never been found to directly displace or combine with *less than* its own weight of any other element or compound, or indeed with less than three times its own weight of any other form of matter; hence it is properly taken as the unit of a scale of equivalents, which really includes all the simple and compound bodies known. On this scale, magnesium, silver, and the compound silver nitrate, occupy the positions assigned to them above.

A familiar illustration will probably render the meaning of the term ‘equivalent’ clear. A single brilliant diamond of purest water, weighing but one grain, has approximately the same *purchasing power* as the weight of

Gold represented by　.　.　3 sovereigns.
Silver　　,,　　,,　.　. 60 shillings.
Bronze (an alloy of tin and copper), by 720 pence.

A diamond of a certain quality will purchase more than its own weight of any other substance : the

economic value of a unit weight of diamond in exchange is therefore greater than that of any other material found in commerce. Similarly the *chemical value* of a unit weight of hydrogen in exchange is greater than that of any other element known to chemists.

As 170 c. grs. of silver nitrate are equivalent to 1 c. gr. of hydrogen, the student will now understand our reason for selecting the weight of the silver compound that we operated upon in the first quantitative experiment.

Experiment 19.—The most convenient method for the preparation of considerable quantities of hydrogen

FIG. 8.
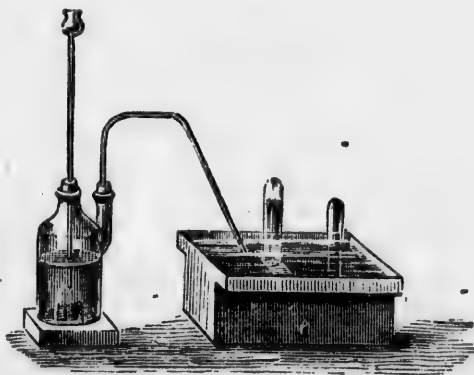
gas for experiment is the following. Take a glass bottle of the form shown in fig. 8, place in it some clippings of sheet zinc and sufficient water to occupy about one-third of the bottle   Replace the cork and pour some oil of vitriol—about a teaspoonful—down the thistle funnel. Chemical action quickly commences and hydrogen gas is freely evolved ; for zinc, like magnesium, easily dis-

places hydrogen from acidulated water—1 centi-
gram of the gas being set free by 32·5 c. grs. or
one equivalent of pure zinc. The gas is conducted by
means of the glass delivery tube under the water in
the 'pneumatic trough,' and it is there collected in
glass jars or bottles previously filled with water and
inverted, keeping the mouths under the liquid in the
trough. A small shelf supports the jars over the
delivery tube. It is advisable to allow the gas to
bubble through the water for some time before collect-
ing it in jars, or until the air is judged to be expelled
from the gas bottle and its place taken by hydrogen,
as the latter forms an explosive mixture with atmo-
spheric air.

a. Remove a jar full of hydrogen from the water,
keeping its mouth downwards. Take a piece of

FIG. 9.

FIG. 10.

lighted taper attached to a wire and pass it rapidly up
into the jar, as shown in fig. 9. The gas takes fire at
the mouth of the tube and burns there with a pale

blue flame, but the taper is extinguished ; on bringing it down to the mouth of the tube again, it can be re-kindled there. Therefore hydrogen, though a combustible gas, *does not support the combustion* of a taper which burns readily in air.

b. Take a dry glass jar, hold it with its mouth downwards and bring under it a jar full of hydrogen, carried from the trough with its mouth downwards. Now invert the jar of hydrogen, bringing its mouth under that of the dry jar, as shown in fig. 10. After ten or fifteen seconds remove the lower jar and bring the lighted taper under the upper one : a slight explosion occurs, and flame is observed, indicative of the presence of hydrogen ; therefore the latter body is so much lighter than air that it can be poured *up* through the latter, and will accumulate in the upper part of any vessel previously full of air.

c. The same point can be elegantly demonstrated by removing the gas delivery tube from the water, drying it, and introducing the end into the neck of a small collodion balloon. If any zinc remains undissolved in the generating flask, a few drops of fresh acid added through the funnel will hasten the evolution of gas, and the latter passing into the ballon will expand it. When fully distended, detach the balloon from the tube and set it free. It will ascend rapidly through the air of the room until arrested by the ceiling, and will remain there until much of the gas escapes and the residual hydrogen is no longer sufficient to buoy up the balloon. The latter then falls and may be reserved for another experiment.

CHAPTER IV

EXPERIMENTS WITH HYDROGEN AND OXYGEN GASES.

Experiment 20.—As we have already proved that hydrogen gas burns in air, we may evidently construct a small apparatus which can afford us a stream of the gas for combustion at a jet. The most convenient form is that represented in fig. 11. The gas delivery tube of fig. 8 is replaced by a short piece of straight tube, which passes through the cork of the generating bottle and through the cork of the wide tube, *t*, which latter is filled with fragments of calcium chloride, a powerful absorbent of moisture. Through the second cork of *t* there passes a small glass tube, drawn out so as to form a rather fine jet. The flask contains strips of zinc, and water, as before, and on pouring oil of vitriol down the funnel tube, hydrogen is evolved. Let the stream of gas issue freely from the jet for some time before a light is applied,[1] else an explosion will occur; then kindle the gas.

Fig. 11.

[1] It is well to cover the jet with an inverted test tube, and to remove the latter, mouth downwards, when it is desired to test the gas, and then to apply a flame to the test tube. If

a. Note that the hydrogen flame is of a pale bluish colour, and emits very little light; but it is intensely hot, for if we introduce a fine platinum wire into the flame it becomes nearly white hot, and emits much light.

b. If we take a glass tube, open at both ends, about one centimeter wide and 30 centimeters long, and pass the jet up into it, the flame is seen to suddenly elongate and a musical note results. The note emitted by this *chemical harmonicum* depends on the diameter and length of the tube; consequently tubes varying in these particulars may be used to produce different sounds.

c. It will be observed in these experiments that the glass tubes are bedewed when they approach the hydrogen flame. Next place the flame under a large bell jar, or invert over it a large dry wide-mouthed bottle. The inner surface of the bottle is quickly bedewed with moisture, and presently drops of liquid trickle down the sides and collect at the shoulder. When some drops of the liquid have been collected, it can be examined, and is then found to possess all the properties of *water*. Now, since the calcium chloride in the drying tube completely removes moisture from the *unburned gas*, and the latter does not bedew a cold surface against which we may allow it to impinge, the liquid we observe to be deposited from the flame must be a product of the combustion of hydrogen in air, just as the white substance, see

the gas burns quietly, it may be safely kindled at the jet; but if with explosion, it is still unsafe, and the testing must be repeated after a few minutes.

Experiment 2, is a product of the combustion of mag-
nesium in air. By means of the next experiment we
can prove that the water produced in the combustion of
hydrogen weighs *more* than the gas burned, and there-
fore that the process is one of chemical combination
in progress between hydrogen and some constituent
or constituents of atmospheric air; the resultant water
is consequently a compound of hydrogen, or of the
water generator (ὕδωρ, water; γεννάω, I generate), with
some other kind of matter.

Experiment 21.--Take a U tube of the form of *a*,
fig. 12, fill the wide limb very loosely with fragments

FIG. 12.
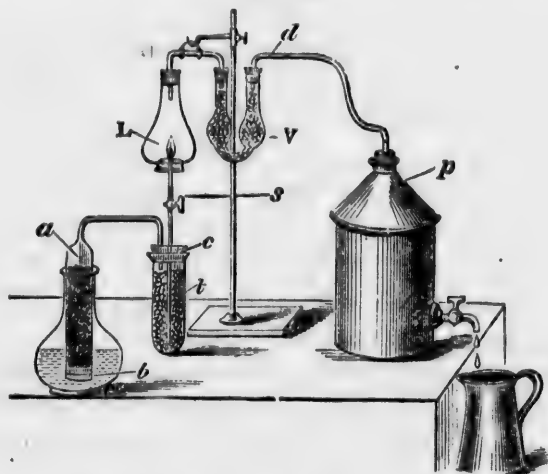
of zinc and insert the cork *b* which serves to prevent
the zinc falling out when the tube is inverted, but
which should be perforated so as to allow liquid to
flow freely in and out. Pass the narrow limb of the
U tube through a good cork *c* which fits a test tube

about 2 centimeters in diameter. The cork also carries the glass tube *s* provided with a fine glass stopcock which can regulate the supply of gas to the jet in which the tube terminates ; the wide end of this tube is sufficiently large to pass through the cork *c* to the bottom of the test tube *t*. The latter is now filled with fragments about the size of a pea of dry and porous calcium chloride, and by turning the tube nearly on its side and tapping, the tube of *s* can be passed down along the glass and the cork inserted as shown. Now pass the wide limb of *a* through the neck of a light flask of about 80 or 100 centimeters' capacity, containing diluted sulphuric acid, and secure the tube *a* in the neck by means of slices of rubber cork, but without interfering with access of air. On turning the stopcock *s* the acid rises in *a* and acts upon the zinc, hydrogen is evolved and passes through the drying tube *t* before it can escape from the jet. The evolution of gas is allowed to continue until all air has been expelled, then the hydrogen can be kindled at the jet, and once it is found to burn freely, the stopcock is turned off, the evolution of gas ceases, because the latter has now no exit through *s*, and accumulates in *a*, forcing out the acid through the perforated cork *b*, and therefore away from contact with the zinc.

Before the experiment, the apparatus is accurately counterpoised, and a quantity of dry gas is then burned at the jet, under conditions to be presently described, and the stopcock again closed. If, when cold, the apparatus be replaced in the balance it will, of course,

weigh less than before, and the weight lost is the weight of dry hydrogen burned.

Another piece of apparatus is now to be prepared. This consists of a small paraffin lamp chimney, L, fig. 12, connected by means of a cork, as shown, with the U tube V filled with calcium chloride. This is our water collector, and is to be attached by the wire hook to the arm of a balance and carefully counterpoised before an experiment.

Conduct the experiment thus : counterpoise both pieces of apparatus and connect *d* by means of a flexible tube with an *aspirator*[1] *p*, as shown, so that a stream of air may be drawn slowly through the water collector during the combustion of the hydrogen. Now turn the stopcock *s*, immediately kindle the hydrogen, and pass the flame well up into the tube L. Water is produced during the combustion and collects chiefly in V. When the hydrogen has burned for some minutes, close the tap *s*, and stop the current of air through L; allow both pieces of apparatus to cool down completely, then disconnect and weigh each separately. The gain in weight of the drying apparatus represents the weight of water produced by the combustion of the weight of hydrogen burned at the jet *s*.

When the experiment just described is conducted

[1] A five-gallon oil can provided with a stopcock, as shown, and its mouth closed by a cork, carrying the inlet tube, forms an aspirator of a convenient size. The can is nearly filled with water at the outset ; when the water is allowed to flow through the tap, air enters through the inlet to replace it, and thus a steady current can be drawn through any apparatus.

with great care, it has been found that for every centigram of hydrogen burned almost exactly 9 centigrams of water are obtained in the drying apparatus ; thus it can be proved that the hydrogen gains in weight on undergoing combustion in air; and, further, that the product of combustion weighs 9 times as much as the hydrogen burned.

The next step clearly is to resolve water into its constituents, or to decompose it, in order to isolate the matter which hydrogen must have obtained from air.

The compound water, whether in the liquid condition, or when gaseous (as steam), withstands a comparatively high temperature without decomposition ; similarly light alone is without action upon it, but electricity is found to decompose it with facility, and the current derived from a Grove's or Bunsen's galvanic battery consisting of two cells is sufficient for the purpose.

Experiment 22.—If we attach to the copper connecting wires of such a battery small slips of platinum (taking care that the connections are perfectly clean and bright), and then plunge the platinum terminals or 'poles' into some water acidulated with a few drops of oil of vitriol, in order to make it a good conductor for electricity, bubbles of gas are seen to rise from each pole. Note that more gas seems to be evolved at the pole connected with the zinc end of the battery than at the other. In order to collect the gas it is only necessary to arrange the apparatus shown in fig. 13. The vessel v contains the acidulated water. The two test tubes are filled

with some of the same water and then inverted with the mouth of each below the level of the water in the

FIG. 13.
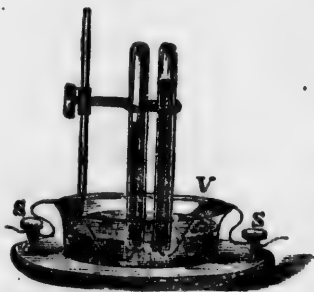
vessel v, and supported close together by clamps. The platinum poles are now arranged as shown, their wires being attached to the binding screws s, s, which latter are also connected with the battery. The wires are dried and then completely coated with sealing wax, from the platinum slip to the point *c*, so as to prevent any escape of electricity, except through the plates, when they are immersed in the water. Each platinum pole is then brought under the mouth of a test tube and secured in position. Gas bubbles arise from the poles as before, but instead of escaping into the atmosphere they collect in the tubes placed to receive them. A marked difference is observed in the amount of gas given off at each pole, and it is presently seen that when one tube is half full of gas the other is but quarter full.

In order to examine the gas in each tube, remove the wires, then close the mouth of the tube containing the largest volume of gas with the thumb passed under the surface of the water in the vessel v. Invert the tube, slip aside the thumb, and quickly apply a flame to the mouth of the vessel ; the gas takes fire and burns with a pale blue flame, and this gas is hydrogen.

A similar experiment is made with the contents of the second tube, but the gas it contains does not take

fire. If, however, we dip into the gas a splinter of wood with a glowing tip, the wood bursts into flame, and active combustion ensues. This gas is, therefore, incombustible in air, but is a *supporter of combustion.* This body, like hydrogen, is an element and is called OXYGEN.

The process of analysis by electricity just used is termed *electrolysis*, and is often employed in effecting the decomposition of chemical compounds. During the electrolysis of water we have already observed that twice as much hydrogen is evolved as oxygen, and the presumption is that those are the proportions by volume in which the two gases unite to form water.[1] But we have not yet proved that water consists of hydrogen and oxygen *only.* If, then, we take the mixture of gases evolved from water, consisting, as we know, of two volumes of hydrogen and one volume of oxygen, such a mixture must be capable of reproducing water *if* the latter consists exclusively of these two elements in the proportions stated.

Experiment 23.—Take a stout wide-mouthed phial of about 100 c.c. capacity. Fit it with a caoutchouc cork and, having bored a hole axially through it, insert the short limb of the narrow but strong delivery tube bent in the form shown at *d*, fig. 14. The wider tube shown can be filled with fragments of calcium chloride when a supply of the dry gaseous

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[1] 100 cubic centimeters of water dissolve only 2·989 c. cs. of oxygen at mean temperature and pressure, and 1·93 of hydrogen gas under the same conditions; the solubility of each gas is therefore so low and so nearly the same, that the above inference may be fairly drawn.

mixture is required. Then pass two stout wires of platinum through the cork on each side of, and close to, the glass tube, and attach small slips of platinum foil to the ends of the wires that project within the bottle. Nearly fill the vessel with water containing a little sulphuric acid and insert the cork, connect the wires projecting from the cork with the terminals of the battery, as shown, and a steady supply of an electrolytic mixture of hydrogen and oxygen will be

FIG. 14.
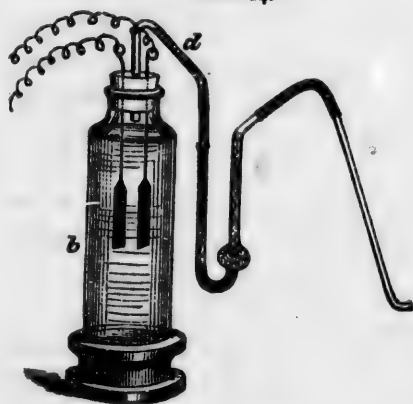
FIG. 15.

obtained. When it is judged that all air has been expelled from the bottle and tubes, collect some of the mixed gases in a small test tube over the liquid metal mercury, contained in a small and strong glass trough, as in fig. 15. This mechanical mixture of the two gases may be kept for an indefinite time without combination taking place, but if we remove the test tube from the trough and apply a flame to the mouth —a flash of light, and a rather violent explosion follow, indicating that chemical union has taken place.

We thus learn that combination of the gases can be determined by heating them sufficiently.[1]

Experiment 24.—A stout glass tube closed at one end is now taken ; it should be about 50 centimeters long and 1 centimeter in diameter. Two thin platinum wires pass through the sides and are sealed into the glass near to the closed end, and opposite to each other ; but their extremities within the tube must be kept at a very short distance apart. The object of this arrangement is to leave a gap so that an electric spark may be sent between the wires within the tube, and thus, by heating the mixture of gases, determine their combination. Such a tube is called a *eudiometer*, and must be stout so as to resist the force of the explosion that ensues ; it is shown at *b*, fig. 15.

Fill the tube with mercury, and when quite full, close the mouth with the thumb, and bring it under the surface of some more mercury, contained in the small trough *t*, fig. 15. Now half fill the tube with electrolytic gases from the apparatus shown in fig 14. Then remove the generator and pass a pad of india-rubber under the mercury and under the mouth of the tube. Press the pad against the bottom of the trough with the tube grasped firmly by the hand. When the tube is in this position, pass a spark from a coil, a Leyden jar, or a small electrophorus, through the gases by means of the wires sealed into the glass, one of them being connected with the earth by means of wire, the other with the apparatus that is to afford the

[1] See Chapter IX. for experiments with the oxyhydrogen flame.

spark. A flash of light passes down the gas in the tube and a jerk is felt by the hand, and then all is over. On relaxing the pressure and moving the mouth of the tube from the pad, but keeping it under the surface of the mercury, the latter rushes up so as to fill the closed end almost completely ; the gases have therefore been condensed,[1] or rather, the product of their union is not a gas, but must be either a liquid or a solid occupying an exceedingly small space as compared with that previously filled by the generating elements. If we examine the upper part of the tube carefully with a lens, we can detect between the mercury and the glass minute drops of liquid. This liquid can be proved to be *water*. It is therefore certain that water consists only of hydrogen and oxygen, and that those elements combine to form water in the proportions by volume indicated by the results of electrolysis.

Experiment 25.—A similar experiment to that just described may be performed with the apparatus shown in fig. 16, termed a 'Cavendish eudiometer,' because it was with such a vessel that the Hon. Henry Cavendish demonstrated the composition of water in the year 1781. The strong glass vessel, fig. 16, is provided with a glass stopcock c and a stopper through which wires of platinum P P pass, and this stopper is retained in the neck of the vessel by means

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[1] As a matter of fact a small bubble of hydrogen remains after explosion ; this is chiefly due to the loss of a little oxygen by solution in the water of the bottle *b*, fig. 14, and further by conversion of a very small proportion of the element into a body called 'ozone.' If all the oxygen were evolved as gas there would not be any free hydrogen after the explosion.

of the clamp A. The brass stopcock B allows the
apparatus to be screwed to the plate of a good air-
pump, and when exhausted of air,
B and c are closed, and not opened
until the tube is screwed to the brass
stopcock of a bell jar similar to
that shown in fig. 18, but containing
some of the electrolytic gases. On
opening the taps the mixture of
gases rushes in to fill the vacuum.
The stopcocks are again closed,
the eudiometer screwed to its stand,
and a spark passed through the
mixture. A brilliant flash of light
accompanies combination, and the
sides of the glass vessel are bedewed

FIG. 16.

with the water resulting from the combination of the
gases.

The experiments hitherto made have led directly
to the conclusions we have already drawn from them
respecting the composition of water, but they also
afford complete proof that atmospheric air contains
oxygen ; and we thus learn in addition that the great
heat evolved during the combustion of hydrogen in
air is due to the chemical union of hydrogen with the
oxygen of the air. Finally, we are led to suspect that
all ordinary cases of combustion which come under
our notice are due to the rapid chemical combination
of atmospheric oxygen with the body burned. Under
Experiment 21 a method was described by which the
weight of water produced during the combustion of
1 c. gr. of hydrogen was determined, and it was stated
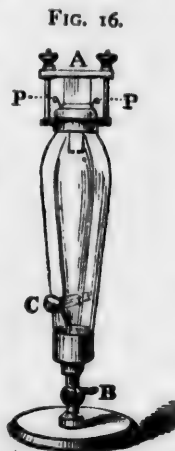
that 9 c. grs. of water resulted. Since we now know that the gain in weight could only be oxygen derived from the air in which the gas burned, the equivalent of Oxygen must be $9-1=8$.

When the metal magnesium burns in air, a white solid only is produced, and it is found that 12 centigrams of. the metal afford 20 c. grs. of the white body, that is to say an equivalent of the element magnesium (12 parts) unites with an equivalent of the element oxygen (8 parts), and produces an equivalent (20 parts) of the compound body termed magnesium oxide or 'magnesia'—for

$$12+8=20.$$

The truth of the statement is not so evident in the case of a candle, for when the latter burns perfectly in air, the matter of the candle is apparently destroyed. But since we know that matter is indestructible, we conclude that the candle is resolved by combination with oxygen into invisible products. These products we can actually collect if we burn a candle in the apparatus, fig. 17.

Experiment 24.—Attach the small paraffin candle c to the perforated cork, and insert in the lamp glass G. The top of the latter is closed by a cork through which a bent tube passes which serves to connect the lamp glass with the U tube. The limb of the latter nearest to the lamp glass is filled with lumps of calcium chloride, and the second limb with fragments of caustic soda   When the cork c is placed in position, the apparatus, with the candle, is attached to one arm of the balance and carefully counterpoised.

The tube *t* is then connected by means of a flexible tube with the aspirator A, and a current of air gently

FIG. 17.
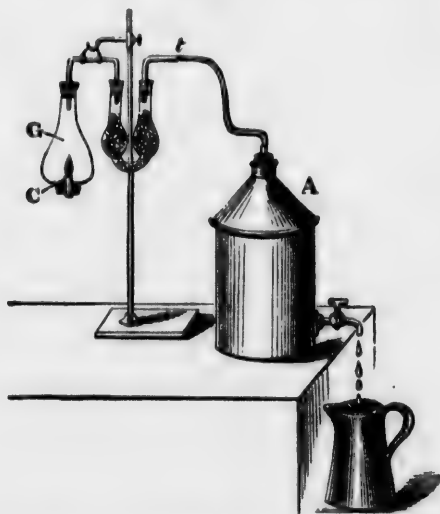
drawn through the apparatus. The candle is removed, lighted and replaced, and then burned within the lamp glass, while the products of combustion are obliged to pass over the absorbent materials in the U tube. When the candle has burned for five minutes or so, put it out and allow the whole apparatus to cool down to the ordinary temperature. Then replace in the balance and observe that the weight has *increased*. Therefore, not only has no matter been lost during the combustion of the candle, but it has actually gained, and, as we shall see at a later stage of our study, the gain represents oxygen derived from atmospheric air, and chemically combined with the matter of the candle during combustion.

CHAPTER V.

EXPERIMENTS WITH HYDROGEN AND OXYGEN GASES
(*continued*).

WE now know positively that oxygen gas is a constituent of atmospheric air—though it is not the only one—and of water. The study of the composition of the latter has further made known the curious fact that oxygen requires twice its volume of hydrogen gas to form water, and only in this proportion does direct combination take place between those elements. Therefore the two gases unite in as definite proportions by volume as by weight, and it is evidently probable that an intimate connection exists between weight and volume combination in this case: hence we must investigate the point more closely.

Experiment 27.—The first step in this direction is to select a globe of about $1\frac{1}{2}$ liters' capacity provided with a stopcock, and to exhaust it of air as completely as possible, by means of a good air pump, to the plate of which it can be screwed; then close the tap securely, remove and counterpoise carefully on the balance. The globe is next taken from the balance and connected, as shown, with a vessel containing pure hydrogen gas, and the stopcock opened, hydrogen rushes in and fills the globe. The stopcock is

again closed, after the levels of liquid within and without the jar have been equalised, and the vessel re-weighed. The increase in weight is that of the hydrogen which has entered. The globe is again ex-hausted to the original point as determined by the gauge attached to the pump, and again filled with gas, but this time with pure oxygen, whose weight is then determined. Now if care be taken to exhaust as completely as possible each time—certainly to the same extent—and that the bodies are pure, and the temperature does not vary so as to unequally expand or contract the gases, the weights obtained are those of equal volumes of the two gases. In a particular experiment con-ducted in this way the hydrogen weighed 11 centi-grams, and the oxygen gas 174 centigrams. The *specific gravity* of oxygen as compared with hydrogen, or *the ratio of the weights of equal volumes of the two bodies*, when hydrogen is taken as the standard, and =1, is

Fig. 18.

$$\frac{174}{11} = 15\cdot 8,$$

or as nearly in the ratio of 1 : 15·96—the true ratio —as can be expected in a rather rough experiment. Therefore oxygen gas may be said to be 16 times heavier than hydrogen. Now since one volume of oxygen requires two volumes of hydrogen for the production of water, it follows that 8 centigrams

by weight of oxygen must unite with 1 centigram of hydrogen to form 9 centigrams of water—a result identical with that obtained by the direct weighing of the water produced in the combustion of a given weight of hydrogen. Therefore, a very close connection exists between combination by weight and by volume.

It may be added that the specific gravities of all gases can be determined by the method just described, and since hydrogen is the lightest gas known, it is taken as the standard for reference.

The experiments already made with the two gases, hydrogen and oxygen, place beyond doubt the fact that they are perfectly distinct forms of matter as far as chemical characters are concerned, but they evidently resemble each other in certain *physical characters*, for they are both colourless, invisible, and inodorous. Let us now see whether this resemblance extends farther.
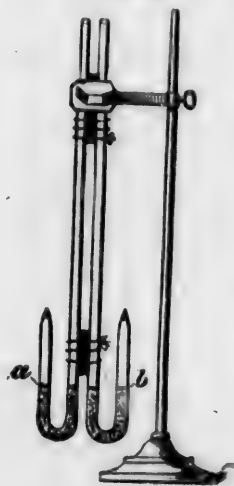
Fig. 19.

Experiment 28.—Take two tubes of as nearly as possible the same diameter and length. Close each at one end and bend to the form shown in *a* and *b*, fig. 19. The short limb may be about 20 centimeters, and the longer 1 meter, in length. Take one of the tubes, fill with water acidulated with dilute sulphuric acid and invert over the pole (fig. 13) from which electrolytic hydrogen is

being evolved; collect enough of the gas to about half fill the shorter limb of the U tube, then close the mouth with the thumb, remove and make the gas pass completely into the closed limb: this can easily be done by bringing the tube to a horizontal position while the shorter limb is uppermost. When the gas has been transferred, bring the apparatus into the position shown, and adjust the level of the liquid in both limbs of the U by sucking out the water in the long limb by means of a pipette with a flexible tube attached, which latter should be of sufficient length to reach nearly to the bend. Fill the second tube to the same extent and in the same manner with electrolytic oxygen, and tie the two tubes securely together as shown.

When the apparatus is plunged up to the point *a* in a large beaker nearly filled with water at the boiling temperature, the gases in the tubes are found to expand considerably. The expansion of the hydrogen is seen to be the same in amount as that of the oxygen. Similarly in cooling down again to the temperature of the air they contract equally.

We learn from this experiment that the two gases resemble each other in another particular, namely, that they are effected *to the same extent by equal alterations of temperature*, when observed under the same conditions.

Now replace the hot water in the beaker by some at the temperature of the room, and leave the tubes undisturbed for several minutes, in order that the gases may acquire the temperature of the water in the large vessel; then pour mercury into each wide tube until nearly full, and the column in each is of equal length.

Note that as the columns of mercury rise to the same level and as the pressure upon the gases equally increases, *they contract to the same extent.*

If we remove the mercury, the gases expand equally and regain their original volume when the pressure is reduced to that at which we commenced.

Therefore hydrogen and oxygen gases, when compared under the same conditions, are affected in the *same way and to the same extent by equal alterations of pressure.* When the same mode of investigation is applied to other gases, whether elementary or compound, they are found to suffer very nearly equal changes of volume when subjected to equal variations of temperature and of pressure.

The conclusion to be drawn from all the data before us is that all gases agree in *physical constitution*, however much they may differ in *chemical composition.* This conclusion is independent of any hypothesis that may be founded upon the facts, but a most important one has been based on them by the distinguished physicist Avogadro. He assumed that all gases (as well as solid and liquid forms of matter) are made up of almost numberless, separate little particles, termed *molecules* (from *molecula*, a little mass), and that *equal volumes of gases contain the same number of molecules, when compared at the same temperature and pressure.* This is the statement of Avogadro's, or, as it is often called, Ampère's law, for to the last-named philosopher is due the credit of having specially drawn the attention of scientific men to the importance of the principle enunciated by Avogadro, when the statement of it made by the latter had been all but

completely overlooked. It follows from Avogadro's law that the ratio of the weights of equal volumes (containing equal numbers of molecules) of hydrogen and oxygen gases, compared at the same temperature and pressure, must represent the relative weights of the free molecules, or ultimate particles, of the two bodies. We have already found (Experiment 27) that a given volume of oxygen is sixteen times heavier than an equal volume of hydrogen under the same conditions : therefore the molecule of oxygen is sixteen times the weight of the molecule of hydrogen.

Let us proceed a step farther. We know already that one volume of oxygen and two volumes of hydrogen gas unite to form the compound water. We may now express the same thing in the following statement :—One molecule of oxygen unites with two molecules of hydrogen to form the compound water. But the question then arises whether one or more molecules of the compound water result from their union. We can obtain an experimental answer to this question in the following way :—

Experiment 29.—Take a eudiometer tube similar to that already employed in Experiment 15, 6 millimeters in diameter, and 80 centimeters in length, and fill it not more than one-third with the electrolytic mixture of oxygen and hydrogen as before ; now place over the tube the glass jacket *j* as shown, which is connected above by a cork with a flask *f*, in which water is boiled and by means of which the jacket can be filled with steam. The lower end of the jacket is also closed by a cork through which the eudiometer passes, and the side

tube *t* which serves to convey away the excess of steam.

When the gaseous mixture in the eudiometer is

FIG. 20.

heated, it expands until it acquires the same temperature as the steam. When the mercury ceases to fall, mark its position in the tube by means of a flexible ring slipped over the jacket, and also measure as accurately as possible the height of the mercury in the tube over the surface of that in the trough *m*, then press the mouth of the tube firmly down on an india-rubber pad, *p*. passed under the mercury for the purpose, and explode the mixed gases as in the former experiment. This can readily be done if the wires fused into the glass sides of the eudiometer are connected with short wires which pass between the cork and the glass jacket, as at *w* and *w'*.
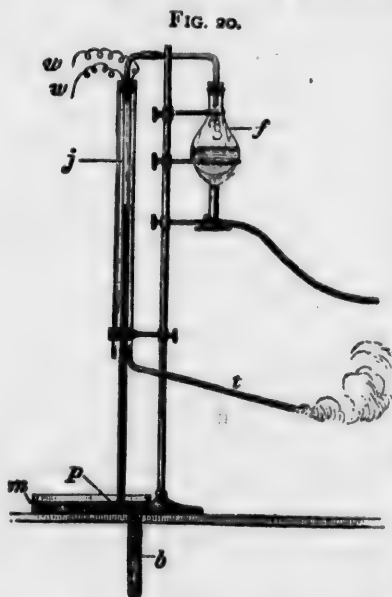
When the pad is removed from the mouth of the tube after the explosion, the mercury is seen to rise in the eudiometer; but, before measuring the amount of contraction that has taken place in the gas, it is necessary to restore the original pressure by depressing

the eudiometer in the well *b*, of the pneumatic trough, until the difference of level between the surface of mercury in the tube and in the trough is the same as before explosion ; it will then be found on measuring the gas (water-gas) remaining in the tube that the contraction amounts to *one-third* of the original bulk of the mixed gases, while the temperature has throughout been maintained by the current of steam.

After explosion we can have but water-gas, or steam, in the eudiometer ; but the steam is prevented by the high temperature and low pressure from condensing to the liquid form. We have therefore measured water-gas under the same conditions as the mixture of two volumes of hydrogen and one of oxygen before explosion, and found that the water-gas occupies the *same space as* the hydrogen which generated it.[1] Now if, as we have seen, the two volumes of hydrogen represent two molecules of that body, the two volumes of the compound water-gas must, according to Avogadro's law, represent *two molecules* of that body. The result may be stated thus in the form of an equation :—

Hydrogen + Oxygen = Water-gas + Water-gas.
2 molecules   1 molecule   1 molecule   1 molecule.

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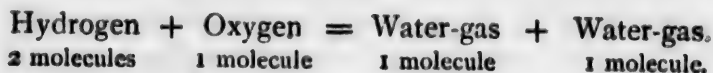
[1] The comparison of the results of a large number of experiments of this order led the illustrious French chemist Gay-Lussac to the following generalisations :—

1. Gases and vapours combine in simple proportions by volume.

2. The volume of a compound gas or vapour always bears a simple proportion to the volumes of gases or vapours from which it has been formed.

Reasoning upon this result, it is perfectly clear that each molecule of wa er-gas so produced must contain oxygen, and, if the law of definite proportions be true, as we know it is, each molecule of water-gas must contain the *same* quantity of oxygen, consequently a semi-molecule of that body. Hence, though the free molecule of oxygen is not divisible by any known physical means, it divides under the influence of chemical attraction into two parts. Now the weight of oxygen corresponding to the semi-molecule of that body is the smallest quantity of it that takes part in chemical change, and as it cannot be further divided, even by chemical means, it is called the *atom*[1] of oxygen.

Later on we shall find that the molecule of hydrogen is also chemically divisible in two parts or atoms.

Now, if the weight of the molecule of hydrogen be taken as $= 1$, the weight of the *atom* of hydrogen must be represented $= \frac{1}{2}$, but since less than 1 part by weight of hydrogen is not known to act in chemical change, it is convenient to take 1 as the *atomic weight*, or weight of the semi-molecule, of hydrogen. The weight of the molecule of hydrogen is therefore $= 2$.

As we have already seen from Experiment 27, the oxygen molecule is sixteen times heavier than that of hydrogen ; therefore, since the molecular weight of hydrogen $= 2$, that of oxygen must $= 32$, while the *atomic weight* of oxygen is 16.

If, then, we desire to know the *atomic weight* of an elementary gas, it is only necessary to find its specific gravity, *i.e.*, to weigh it as in Experiment 27 against an

[1] ἄτομος, indivisible.

equal volume of pure hydrogen under the same con-
ditions. The weight obtained, referred to hydrogen
as the unit, is the atomic weight of the body.

But the information that our experiment affords us
does not end here, for we can deduce from it the
specific gravity of water-gas, referred to hydrogen as
our standard.

We have already learned that two molecules of
water-gas, which must contain the hydrogen in two
molecules (*i.e.*, 4 atoms) of that body, and the oxygen
in one molecule (*i.e.*, 2 atoms) of that element, occupy
the same volume as two molecules of hydrogen.
Therefore one molecule of water-gas occupies the
same volume as one molecule of hydrogen. Now,
one molecule of water-gas must have the relative
weight 18 (16, weight of the semi-molecule of oxygen
+2, weight of the molecule of hydrogen) referred to
the hydrogen molecule=2 ; this gives the ratio of
9 : 1 ; therefore 9 is the specific gravity of water-gas
compared with hydrogen gas as the unit.

It may be useful to add the following definitions :—

A *molecule* of an element or compound is the
smallest portion of a body that can exist in the *free
state*.

An *atom* of a chemical element [1] is the smallest
portion of it that is known to take part in chemical
change, and is almost invariably the semi-molecule.

An *equivalent* of an element or compound is its
replacing or combining value compared with an unit
weight of hydrogen.

The Atomic Theory of the illustrious philosopher,

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[1] A chemical compound has not atomic weight.

Dr. John Dalton, of Manchester, was one of the first substantial attempts [1] to account for the law of definite proportions that we have seen to so remarkably govern chemical changes, and we may now state the theory and the difference in form between it as enunciated by Dalton (in 1804–8), and as adapted to the present state of our knowledge. Dalton supposed, as Avogadro did, that with all matter a point can be reached at which further mechanical subdivison is impossible, and it was to these ultimate particles he applied the term *atom*—the atomic weight being a constant for each element. The molecules of the present day are the representatives of the atoms of Dalton, and we have already learned from our experiments that the molecule of an element, though physically indivisible as we suppose, can divide under the influence of chemical attraction into two—but rarely more or less than two—parts, and to each part we now apply the term *atom.* Dalton further assumed *that chemical action takes place only between the atoms of matter, and in proportions by weight which are determined by the relative atomic weights of the elements.*

In the Daltonian theory as thus modified we have an explanation of the law of definite proportions, but it is necessary to guard against the supposition that the law of definite proportions *depends* on this hypothesis. As we have seen, the theory is founded on two assumptions, both reasonable, it is true, but which are not at present capable of direct proof. We

[1] The fundamental conception in the ‘Atomic Theory’ was distinctly enunciated by two Dublin chemists—Kirwan in 1783, and Higgins in 1789.

may, therefore, use the theory as an important help in our inquiries, but not as a support on which we may rest in full confidence. If, however, we desire to go still farther, and to enquire how it is that these elementary atoms possess the power of uniting with each other, we must simply confess that this is one of the many mysteries that still lie hidden from the view of man.

CHAPTER VI.

EXPERIMENTS WITH THE METALS, SILVER, COPPER, AND MAGNESIUM.

It is obvious that the method of weighing an element in the form of gas against the same volume of hydrogen, when we desire to determine atomic weight, is only applicable in those cases in which the element is either a gas at ordinary temperature and pressure, or in which it can be converted into gas, or vapour, at a moderate and manageable degree of heat. Neither silver nor magnesium can be vaporised at even moderately low temperatures: hence we must seek for some other mode than that above referred to of fixing their atomic weights. The *equivalent*, or replacing value of silver stated in terms of the hydrogen unit, we have already proved to be 108, and that of magnesium 12. Now it is evident that the atomic weight in each case cannot be *less* than those values, but it may be more, for we have already seen that in the case of oxygen the least weight of that body that takes part as a whole in chemical change (the atom) is *twice* the equivalent.

Experiment 30.—Make the following curious and instructive experiment. Take a five shilling piece [1]

[1] Although the coin is not pure silver, it is sufficiently pure for this rough experiment.

and fasten it securely to a piece of fine binding wire.
Take a piece of copper of the *same weight* and thick-
ness, and attach it to wire. Now, while holding the
wires dip the two pieces of metal into some water
boiling in a kettle, or other vessel. After ten minutes
or so remove the pieces, let them drain for a few
seconds and attach the wires to a rod. At first the
metals are equally hot to the fingers, for they have
evidently been heated to the same extent; soon,
however, the silver will be cool enough to be held
between the fingers, and to be pressed against a
piece of phosphorus without igniting it, while the
copper will be still too hot to hold, and will easily
kindle a test of the same kind. The silver, there-
fore, cools more rapidly than the same weight of
copper under the same conditions. As the two
metals do not differ materially in conducting power,
we infer from this experiment that silver at 100° C.
(the temperature of boiling water) contains less heat
than the same weight of copper at the same tempera-
ture—in other words, a less *quantity* of heat is re-
quired to raise the temperature of a given weight of
silver to the same extent as an equal weight of copper,
hence the *capacity* of copper for heat is greater than
that of silver.[1] If we could conveniently replace the

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[1] That is to say the *specific heat* of copper is greater than
that of silver. Water has the greatest capacity for heat of any
liquid or solid, and the heat capacity of other bodies is
referred to that of an *equal weight* of water as unity : thus the
capacity of silver for heat is about $\frac{1}{17}$th that of an equal weight
of water, the precise ratio being ·05701 : 1. This ratio is
the *specific heat* of silver. The *atomic heat* of an element is

copper by the same weight of magnesium, the difference in rate of cooling would be still more marked. This difference amongst solid bodies in capacity for heat has long been known, but it remained for two eminent French physicists, MM. Dulong and Petit, to point out the fact that the elements having the highest equivalents are those of the lowest capacity for heat, and *vice versâ*, and they showed from numerous observations that *the heat capacity of an element is inversely as its equivalent.* This 'law of Dulong and Petit' attracted comparatively little notice until Professor Cannizz... ...fied the statement of it, and drew atter... ... its great value as serving to aid the determination of the atomic weights of many of the solid elements.   The law, as it now stands, may be stated thus:—*The atoms of elementary matter have the same capacity for heat.*

If this law be true, 108 centigrams of pure silver and 12 centigrams of pure magnesium when heated to 100° C.—the temperature of boiling water—and then allowed to cool, ought to give out on cooling to the same extent *the same quantity of heat*, if the above numbers represent the relative weights of their atoms.

Experiment 31.—By the method now to be described we can apply this test to the two metals.

The *atometer*, fig. 21, is really a large spirit thermometer with a test tube inserted in the bulb, as shown, and hermetically sealed therein.   The shaded portion is full of alcohol, coloured red in order to

the product of the specific heat by the atomic weight, and is about 6·0.   Thus ·05701 × 108 = 6·157.

make its motions in the stem more evident. The stem
s should be about 30 centimeters long, graduated
clearly in milli-
meters. The in-
strument ought to
be so constructed
that the thread of
liquid should ad-
vance through a
length of fully 30
millimeters for an
increase in tem-
perature of one
degree centigrade.
The bulb of the
atometer is bed-
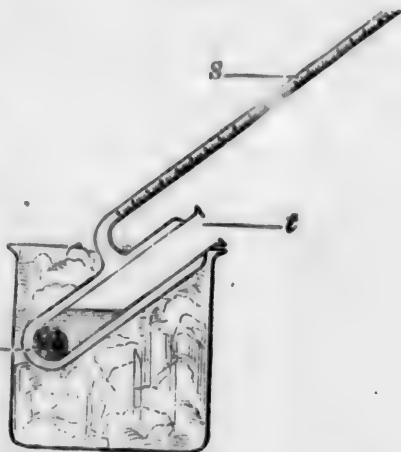
Fig. 21.

ded, as shown, in cotton wool contained in any con-
venient beaker, or better still, a heavy tumbler. A
small piece of cotton wool is passed down to the
bottom of the test tube *t*, and one cubic
centimeter of water accurately delivered into
the previously dry tube from a measuring
pipette, or dropping tube, fig. 22. The whole
apparatus is left in a cool place until the thread
of liquid in the stem becomes steady, *i.e.*
until the instrument acquires the same tem-
perature.

Fig. 22.

Now take a piece of pure metallic silver
weighing exactly 1 centigrams, and of
such a shape that it can easily pass into the
test tube *t* of the atometer. Place the centigram
atom of silver in the test tube *h*, which passes rather

loosely through the cork of the flask *f*, fig. 23. The test tube should be closed by a small stopper of cork

FIG. 23.

or vulcanite. Through the cork of the flask another tube passes which is open at both ends, and which gives exit to the current of steam produced when the water in the flask is boiled vigorously. The test tube and the contained silver are thus heated to the temperature of steam, *i.e.* 100° C. if the pressure be 760ᵐᵐ. After ten minutes heating in the steam bath the metal will have acquired the desired temperature: then remove the tube *h* quickly, bring its mouth near to the mouth of the tube *t* of the atometer, withdraw the cork *i*, and so invert *h* that the lump of silver *s* may quickly drop into the water in *t*, where it parts with its heat. The little piece of cotton wool prevents the lump of silver from breaking the glass.
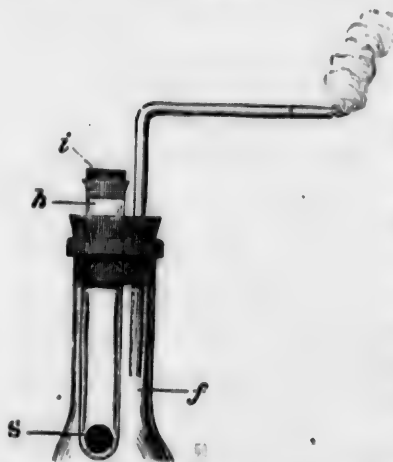
If the temperature, as indicated on the stem *s*, be noted just before the introduction of the silver, the thread of liquid will be seen to rise almost immediately after the silver has been dropped in, and will continue to rise until it reaches a maximum.

In an experiment made in this way the thread of liquid in the atometer rose from 10 to 39 (29 divisions) after the 108 c. grs. of silver had been introduced.

Now take 12 centigrams of pure magnesium in *lump*, not ribbon, place it in the tube *h*, and heat it to 100° C. in the same way as the silver.

While the magnesium is heating, pass a wire with a hook at the end into the tube of the atometer, and raise nearly to the mouth of *t* the piece of cotton wool which will carry with it the lump of silver. After the water has drained away from the latter, pick out the silver with a forceps and push the cotton back under the water, then remove the wire. At this time the liquid in the stem *s* will be still above the point from which it started in the experiment with silver, therefore remove the bulb *c* and blow upon it, or so cool it as to get the thread contracted to a lower point than we require; now replace in the wool, and allow the temperature to gradually rise, until the silver starting point is reached. By this time the magnesium will have been heated to 100° C., and it is now to be plunged into *t*, as in the former experiment, and the rise in temperature noted.

In the particular experiment above referred to, the liquid expanded from 10 to only 25 (15 divisions) or to little more than *half* the extent that it did in the case of 108 c. grs. of silver.

The conclusion we draw from this result is that 12 c. grs. of magnesium at 100° C., contain but half the quantity of heat that 108 c. grs. of silver do at the same temperature. We therefore infer that the weight of magnesium that would contain the same quantity of heat at 100° C. as 108 c. grs. of silver is 24 c. grs., and on repeating the experiment with this larger weight, and under the same conditions as before, we get an

expansion which is nearly equal to that caused by the silver. Now, according to our definition of the term equivalent, silver cannot have a *less* atomic weight than 108; neither can it be *greater*, because the product of the equivalent into the specific heat of silver (see foot-note, page 57.) gives the number 6·157, which accords, within narrow limits, with the *highest product* similarly obtained with any element whose atomic weight can be independently fixed by means of Avogadro's principle. Hence the weight of a solid element that contains at 100° C. the same quantity of heat as 108 parts of pure silver at 100° C. is the atomic weight of the body.

Therefore, according to Cannizzaro's modification of Dulong and Petit's law, 24 is the *atomic* as distinguished from the equivalent weight of magnesium.

It is right to add here that several exceptions are known to this and the preceding law, but these will be dealt with in the proper place.

CHAPTER VII.

TABLE OF ATOMIC WEIGHTS—EXPERIMENTS WITH METALS AND NON-METALS.

THE annexed table contains a list of the principal chemical elements already recognised, and appended to each is the atomic weight which has been determined in most cases by appeal to the criteria employed in the course of our experiments. Opposite to the name of each element is placed a *symbol* by which it is indicated. The symbol for an element is in each case derived from either the English or Latin name of the particular body. Thus H is the symbol for Hydrogen, O for Oxygen, N for Nitrogen, Ag for Silver (from Argentum), Au for Gold (from Aurum).

When the same letter stands at the beginning of the name of more elements than one, *two* letters form the symbol; thus, B stands for Boron, Ba for Barium, Bi for Bismuth, Br for Bromine, and Be for Beryllium.

The symbol for an element when used alone always signifies *one atom* of the body: thus, if we take the centigram as our unit, H signifies *one* centigram of Hydrogen; O, *sixteen* c. grs. of Oxygen; Ag, *one hundred and eight* c. grs. of Silver, and Mg, *twenty-four* c. grs. of Magnesium. The elements are arranged in alphabetical order in the table, but it is usual to

Name	Symbol	Atomic Weight
Aluminium	Al^{iv}	27.3
Antimony (*Stibium*)	Sb^v	122.0
ARSENIC	As^v	75.0
Barium	Ba$''$	137.0
Beryllium	Be$''$	9.2
Bismuth	Bi$'''$	210.0
BORON	B$'''$	11.0
BROMINE	Br$'$	80.0
Cadmium	Cd$''$	112.0
Calcium	Ca$''$	40.0
CARBON	C^{iv}	12.0
CHLORINE	Cl$'$	35.5
Chromium	Cr^{vi}	52.4
Cobalt	Co^{iv}	58.6
Copper (*Cuprum*)	Cu$'$	63.0
FLUORINE	F$'$	19.0
Gold (*Aurum*)	Au$'''$	196.2
HYDROGEN	H$'$	1.0
IODINE	I$'$	127.0
Iron (*Ferrum*)	Fe^{iv}	56.0
Lead (*Plumbum*)	Pb^{iv}	207.0
Lithium	Li$'$	7.0
Magnesium	Mg$''$	24.0
Manganese	Mn^{vi}	55.0
Mercury (*Hydrargyrum*)	Hg$''$	200.0
Nickel	Ni^{iv}	58.8
NITROGEN	N^v	14.0
OXYGEN	O$''$	16.0
PHOSPHORUS	P^v	31.0
Platinum	Pt^{iv}	196.7
Potassium (*Kalium*)	K$'$	39.1
SELENIUM	Se^{iv}	79.0
SILICON	Si^{iv}	28.0
Silver (*Argentum*)	Ag$'$	108.0
Sodium (*Natrium*)	Na$'$	23.0
Strontium	Sr$''$	87.2
SULPHUR	S$^{iv\ or\ vi}$	32.0
TELLURIUM	Te^{iv}	128.0
Tin (*Stannum*)	Sn^{iv}	118.0
Zinc	Zn$''$	65.0

divide them in two great groups, of METALS and NON-METALS, respectively. The names of the former are printed in the table in strong Egyptian type, and those of the latter in capitals, in order to facilitate reference.

The most strongly marked members of each class admit of easy distinction.

Experiment 32.—Take a slip of copper, about ten centimeters long, and a roll of 'cane brimstone,' or sulphur, of the same length. Compare them and note:—

a. That the red-coloured copper exhibits that peculiar *lustre* termed metallic, while the yellow sulphur has a greasy lustre of a perfectly distinct kind.

FIG. 24.
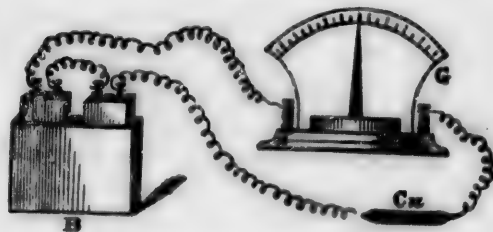
b. That when one end of each specimen touches the surface of some boiling water, the fingers which grasp the other end quickly feel the heat *conducted* by the copper, while those holding the sulphur have not any sensation of warmth conveyed to them.

c. That the copper, *Cu*, fig. 24, when used to connect the terminal wires of the galvanic battery B with the galvanometer G in the circuit, *conducts* the electricity along it, as shown by the strong deflection of the needle. When the copper is removed,

F

and the wires connected by sulphur, the needle is *not* affected.

The metal copper is therefore distinguished from the non-metal sulphur—by the metallic *lustre*, and by conducting *heat* and *electricity* freely.   These broad distinctions are sufficient for the present, but it must be stated that the members of each group cannot all be so sharply defined, and in some few cases it is by no means easy to determine whether in the free element—arsenic, for example—we have to deal with a metal or with a non-metal.

Experiment 33.—Again, take some crystals of 'blue vitriol,' or copper sulphate, and dissolve them in some hot water; now plunge into the solution two platinum slips attached to the terminal wires of a strong galvanic battery.   Immerse for a minute or so, and observe that bubbles of gas separate from one of the plates; withdraw the slips, and note that a red deposit of metallic *copper* is obtained on the slip connected with the zinc end (the negative pole) of the battery.   No deposit takes place at the other pole, but it was from this that bubbles of gas were separated, and this gas could be shown to be oxygen if collected and tested.

We learn, then, that when a compound of copper with a body which certainly contains oxygen is electrolysed, the *metal* makes its appearance at the *negative pole, i.e.,* that connected with the zinc end of the battery.   The reason commonly assigned for this selection of the negative pole by the metal is, that the latter *being electro-positive* is most strongly attracted by the unlike pole, while the non-metal, oxygen, being *electro-*

negative, makes its appearance at the unlike, in this case the positive pole. This is true, not only of the copper compound, but of other compounds of a metal with a non-metal, when subjected to electrolysis; thus while the metals are electro-positive elements, non-metals are electro-negative.

Experiment 34.—Make a fresh solution of copper sulphate and place it in a phial; suspend a clean strip of iron wire in the liquid by means of a string fastened to the cork of the bottle.[1] A deposit soon forms upon the iron, and if the bottle be shaken it falls to the bottom; when the iron is taken out of the liquid it is seen to be coated with copper, and the deposit in the bottle is metallic copper. This action goes on until all the copper has been separated from the solution by the iron, the latter metal dissolving in the liquid. Metallic iron therefore displaces copper from solution without the assistance of a battery.

Experiment 35.—Next dissolve a small quantity of the poisonous 'corrosive sublimate,' or mercuric chloride, in hot water in a test tube, and plunge into the liquid a clean strip of copper. The latter soon becomes coated with a greyish deposit, and if we remove the copper, wash it with water and rub it, a bright silvery surface is obtained due to the separation of the metal mercury, or quicksilver, from the solution by the copper—the latter metal dissolving.

Experiment 36.—Again, dissolve a few crystals of silver nitrate in some water in a small phial, and pour a few drops of pure liquid mercury, or quicksilver, into

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[1] Or plunge a clean steel knife into the liquid.

F 2

the solution, and allow the latter to stand for a day or so. At the end of that time beautiful needle-like crystals of metallic silver will be seen in the liquid, separated out from the solution by the mercury.

We thus learn that the metals are not equally electro-positive, thus iron being more electro-positive than copper displaced the latter from the solution; for a similar reason copper displaced mercury, and mercury the silver.

Experiment 37.—The displacement of silver by magnesium already effected in Experiment 14, is

Fig. 25.

another case in point, and the well-known 'lead tree' is a further illustration. In order to prepare the latter, dissolve about twenty grams of 'sugar of lead,' or lead acetate, in half a liter of water and place the solution in a white glass flask. Secure a piece of clean zinc to a string and suspend the metal in the solution as shown (fig. 25). The metallic lead separates from the solution after some hours in beautiful plates or leaves, while the zinc slowly dissolves.

From the results of experiments of the kind just described, we can draw up the following table of fourteen metallic elements arranged in electro-chemical order. Each metal is electro-positive to those above, and electro-negative to those below it in the list.

Electro-negative.

Gold.	Lead.
Platinum.	Iron.
Silver.	Zinc.
Mercury.	Magnesium.
Copper.	Calcium.
Bismuth.	Sodium.
Tin.	Potassium.

Electro-positive.

This order is subject to some variation with the nature of the liquid in which the experiments are made.

We now return to the symbols of the elements, and have to inquire to what uses they are put in expressing chemical changes.

With the symbols we can build up the 'formula,' of any definite chemical compound, and such an expression informs us of what kinds of matter the body is composed, and in what proportions the several constituents are present. Thus the formula NaCl expresses the composition of common salt, H_2O that of water, and $AgNO_3$ that of silver nitrate.

If we desire to find the formula by which the composition of common salt is to be expressed, we have to ascertain in the first instance of what elementary forms of matter it consists. With the aid of the methods of *qualitative analysis* we can prove that it consists of the two elements, sodium and chlorine. Our next step is to find the proportion of each element present, and this is accomplished by

the methods of *quantitative analysis*, and the results are stated below in percentages.

100 parts of common salt afforded on analysis :—

Chlorine	.	.	.	.	60·62
Sodium .	.·	.	.	.	39·38
					100·00

These are facts, quite apart from any hypothesis; but in order to find the relative number of atoms of each element present in the compound, we divide the percentage of each constituent by its atomic weight, thus—

$$\frac{60\cdot62}{35\cdot5^*}=1\cdot7 \quad \text{and} \quad \frac{39\cdot38}{23\dagger}=1\cdot7$$

Hence there is an equal number of atoms of each element in the compound, and the ratio of Na to Cl is 1 : 1.   The formula of the body is, therefore—

1Na : 1Cl,   or, more simply,   NaCl,

for each symbol represents one atom of the element, and the approximation of the symbols without any sign between indicates that the definite compound, called common salt, is the product of the chemical union of the two elements sodium and chlorine. The chemical name of this compound is *sodium chloride.*

Again, 100 parts of water afforded on analysis—

Hydrogen	.	.	.	11·11÷ 1=11·11 or 2.
Oxygen	.	.	.	88·89÷16= 5·55 or 1.
				100·00

---

* The atomic weight of chlorine.
† The atomic weight of sodium.

or, dividing by the lowest term, 2 atoms of hydrogen to 1 atom of oxygen, and this is expressed by the formula –

$$H_2O;$$

H_2 in this formula indicates two atoms of hydrogen. The chemical name of water is hydrogen monoxide.

Finally, 100 parts of silver nitrate afforded on analysis—

Silver	.	.	$63.52 + 108 =$	.5881 or 1.
Nitrogen	:	.	$8.23 + 14 =$	.5878 „ 1.
Oxygen	.	.	$28.25 + 16 = 1.7656$	„ 3.
			100.00	

The quotients, .5881 and .5878, are so nearly equal that we may fairly set down the slight difference between them (.0003) to unavoidable errors of experiment; it is therefore a matter of indifference which term we employ to divide 1.7656. In either case the quotient is as nearly as possible 3. Hence while we have the same number of atoms of silver and nitrogen in the compound, we have 3 times the number of atoms of oxygen, and these atomic ratios are expressed by the formula—

$$Ag\ NO_3.$$

It often happens that we are given only the chemical formula of a body, and are required to find what its percentage composition must be. The solution of this problem is exceedingly simple, and is always effected by the method we shall now illustrate in the case of silver nitrate.

The first step is to find the *molecular weight* of the

body, *i.e.* the sum of the atomic weights of its consti-
tuents—thus :—

$$Ag \quad . \quad . \quad . \quad . \quad = 108.$$
$$N \quad . \quad . \quad . \quad . \quad = 14.$$
$$O_3 \, (16 \times 3) \quad . \quad . \quad = \underline{48.}$$
$$\text{Weight of molecule} \quad . \quad = 170.$$

Three sums in simple proportion then obtain the
desired information.

$$170 : 100 \therefore 108 : 63 \cdot 52 \text{ the percentage of Ag.}$$
$$170 : 100 \therefore 14 : 8 \cdot 23 \qquad \text{,,} \qquad \text{,,} \qquad N.$$
$$170 : 100 \therefore 48 : \underline{28 \cdot 25} \qquad \text{,,} \qquad \text{,,} \qquad O.$$
$$\underline{100 \cdot 00}$$

The symbol $AgNO_3$ is called an *empirical* formula,
because it expresses only the atomic ratios of the con-
stituents, and does not convey any idea as to the way in
which the elements are grouped within the molecule.
If however we write silver nitrate thus,

$$Ag - O - NO_2,$$
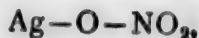
we seek to convey the idea that the atom of silver is
united by means of one oxygen atom to an oxygenated
group, NO_2, and this is termed a *rational* formula.
We shall presently meet with many such expressions.

If we examine lists of chemical formulæ, we can
easily select a number of examples, such as the
following :—

Formulæ.			Names.
1. HCl	.	.	Hydrogen Chloride.
HF	.	.	Hydrogen Fluoride.
2. H_2O	.	.	Hydrogen Monoxide.

Formulæ.			Names.
3. $AuCl_3$	.	.	Gold Trichloride.
4. CCl_4	.	.	Carbon Tetrachloride.
5. PCl_5	.	.	Phosphorus Pentachloride.
6. MnF_6	.	.	Manganese Hexafluoride

All these compounds are *binary* compounds, or those containing only two kinds of matter; when three distinct elements unite, they form a *ternary* compound, as silver nitrate, $AgNO_3$. It is to be noted that the termination of all the above names is the syllable *ide*, and this occurs only in the names of *binary* compounds. Again, the symbol written to the left hand in each formula is that of the *most electro-positive constituent*, and this is also a general rule, though there are some exceptions to it. Lastly, the number of atoms of the electro-negative constituent in the molecule is indicated by the prefixes mono-, di-, tri-, tetra-, penta-, and hexa-.

But the consideration of these formulæ leads us another step forward, for we perceive that the elements H and Cl, as well as H and F, combine atom for atom (and as a matter of fact, in no other proportion), and are therefore said to be equal in chemical power. But a single atom of oxygen can attract and attach to itself *two*, but not more than two, atoms of hydrogen, as in water. Again, one atom of the metal gold can enchain, as it were, three, but not more than three, atoms of chlorine, as in gold trichloride. Similarly, one atom of carbon can fix the maximum number of four atoms of chlorine, as in carbon tetrachloride; the single phosphorus atom, five of chlorine, as in the penta-
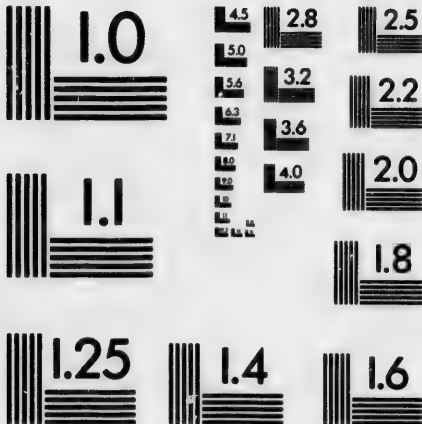
MICROCOPY RESOLUTION TEST CHART

(ANSI and ISO TEST CHART No. 2)

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4.5   2.8   2.5
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5.6   3.2   2.2
6.3
7.1   3.6
8.0
9.0   4.0   2.0

1.8

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chloride; and the manganese atom, six of the element fluorine.

We thus learn that the atoms of the elements differ widely in chemical power. The *atom* of manganese resembles in this respect an open chain of six links, each one of which can attract and hold strongly one atom of the element fluorine; phosphorus, a five link chain; carbon, one of four links; gold, one of three; oxygen, one of two; while the hydrogen, chlorine, and fluorine atoms are represented by single links.

We can thus divide all the known elements into those whose atoms are

1 link, or	Monad,	like	Hydrogen.
2 „	Diad	„	Oxygen.
3 „	Triad	„	Gold.
4 „	Tetrad	„	Carbon.
5 „	Pentad	„	Phosphorus.
6 „	Hexad	„	Manganese.

This hydrogen or chlorine fixing power of an element is often spoken of as the 'atomicity,' 'quantivalence,' or 'valence,' of its chemical atom, and is thus indicated in the symbols by the marks shown :—H', O'', Au''', C^{iv}, P^{v}, Mn^{vi}.[1]

But the atom of an element does not always act with its full chemical effect : thus nitrogen acts as a pentad in sal ammoniac, NH_4Cl, as a triad in ammonia, NH_3, and as a monad in nitrous oxide, N_2O, or laughing gas. Returning to our simile of the chain,

---

[1] The atomicity of each element is marked in the Table of Atomic Weights.

we say that the five link nitrogen atom may also act
with but three links or one, the other links (*i.e.* centres of
attraction, ' bonds,' ' equivalents,' or ' atomicities ') be-
coming latent or inactive *in pairs*, owing to mutual sa-
tisfaction. If we regard the atom of nitrogen as a chain
of five equivalents or links, we can easily illustrate
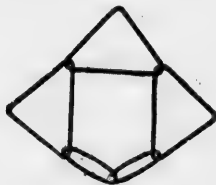the suppression of links in pairs.

Let the following diagram represent the nitrogen
atom, acting as a *pentad*, by an open chain of five
links, each one having but a single *free* point of
attachment, *i.e.*, at a bend or angle ; the chain should
therefore consist of oval and triangular links.

FIG 26.

If we close the chain by connecting the oval links,
thus—

FIG. 27.

three points of attachment are still free, and we have
a representation of the atom of nitrogen acting as an
apparent *triad*.

The next diagram represents the monad condition
of the nitrogen chain, in which but one bend remains
free for attachment.

The disappearance of the points of attachment in
pairs is thus seen to be a mechanical ne-

Fig. 28.

cessity in the case of the links of the
chain.

A triad element, such as gold, would
be represented as a chain of three links
—one triangular and two oval, and this
chain when closed would represent a seem-
ingly monad gold atom, thus—

Fig. 29.

We are acquainted with a number of compounds, in
which the gold atom acts as a monad element.

An element which is never more than a monad,
such as hydrogen, is best represented as a single
circular link, as it has but a single centre of attrac-
tion.

In this way we can symbolise the elements of
uneven atomicity, or *perissads*. The atoms of elements
of even atomicity, or *artiads*, may be represented in a
similar way. Thus the manganese atom acting as a
hexad—

Fig. 30.

as a tetrad—

FIG. 31.

as a diad--

FIG. 32

The element carbon is a good example of a tetrad atom, and may be represented by a chain of two triangular and two oval links; the closed chain corresponds to the carbon atom acting as a diad.

An element which is always diad can be best represented by a chain of two *oval* links, as in the next figure, in this we represent the composition of the molecule of water, which, as we have already seen, contains one atom of oxygen in union with two atoms of hydrogen.

FIG. 33.

The circular links are atoms of hydrogen, while the pair of oval links represent the atom of oxygen.[1]

Such representations of monad, diad, triad, &c., elements may be easily made in a short time by cutting some stout copper wire into equal lengths of about 10 centimeters, and bending each into one or other of the forms of link given above. The links can then be permanently coupled up into chains so as to represent atoms ; and the latter can be employed in illustrating chemical combinations in the way already pointed out.

In using these aids to study, the beginner must carefully avoid regarding them as representations of atomic structure, or, in fact, as other than mere artificial aids.

The student will do well to attach the 'atomicity' marks, as in the table, to all chemical symbols, as he will thus become soon familiar with the replacing and combining values of the atoms.

The symbols as written are evidently capable of use in the explanation of chemical changes, and the latter are in fact represented by *chemical equations.* Thus the equation—

$$2H' + O''* = H'_2O''.$$
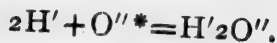
is intended to represent that two atoms of H and one

---

[1] The free molecules of the elements containing two atoms may obviously be represented by two systems of links, so united that every link of each chain is fully engaged.

* The *plus* sign + signifies 'added to,' or 'when made to act chemically upon.' The sign of equality =, stands for the word 'produce.'

of O, when brought together under the proper conditions, unite, and produce the compound water. The number of atoms of each kind of matter on one side of an equation must evidently be equal to that on the other, hence we say—*the weights of the product or products, of a given change, must be equal to the sum of the weights of the bodies taking part in the reaction.*

Again—

$$H'_2O'' = O'' + 2H'$$
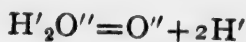
indicates that the compound water has suffered decomposition, and that the products are one atom of O and two atoms of H. In other words, 18 c. grs. of water can afford on decomposition 2 c. grs. of H, and 16 c. grs. of O.

These examples are sufficient for the present, but many others will be given as we proceed. It must be added, however, that the student should not look upon every equation that complies with the above rule as being necessarily a correct one; it must not only equate, but represent the facts as accurately as possible: therefore the quantitative experimental test is the only true one of the accuracy of an equation.

CHAPTER VIII.

EXPERIMENTS WITH ACIDS, ALKALIES, AND SALTS.

Experiment 37 *b*.—Take some common hydrochloric, or 'muriatic' acid, dilute it with about twenty times its volume of water. Note that the liquid has a *sour taste*,[1] and that a piece of *blue litmus* paper is reddened when dipped into the liquid. Then add a small quantity of common 'bread soda,' and note that brisk effervescence takes place, much gas being evolved.

Experiment 38.—Take some *aqua fortis*, or nitric acid, and dilute it to the same extent as the former acid with water. Note that it also tastes sour, reddens litmus, and causes effervescence when bread soda is added to it.

Experiment 39.—Again, take some 'oil of vitriol,' or sulphuric acid, and dilute it with twenty times its bulk of water, adding the strong acid *to the water* drop by drop, and stirring with a glass rod. This solution is also sour, reddens litmus, and sets up effervescence when bread soda is added to it.

If we extended our experiments to all known acids which are soluble in, or can be easily mixed with, water, we should find them to possess in a greater or less degree the characters detected in the

[1] Like vinegar, which contains a body called acetic acid. All strong acids must be cautiously handled, as they are generally corrosive.

three acids tested. The formulæ of these acids are given below—

$$HCl \quad . \quad . \quad . \quad . \quad \text{Hydrochloric acid.}$$
$$HNO_3 \quad . \quad . \quad . \quad \text{Nitric acid.}$$
$$H_2SO_4 \quad . \quad . \quad . \quad \text{Sulphuric acid.}$$

Experiment 40.—Dissolve a piece of 'caustic soda,' or sodium hydrate, the size of a grain of barley, in nearly a test tube full of water, and mix the liquid thoroughly by closing the mouth of the tube with a thumb and shaking. When the solid has quite dissolved, note that the solution has a somewhat earthy taste ; that it does *not* redden blue litmus paper, but *restores* the colour of the paper already reddened by an acid. The addition of a diluted acid does not cause any effervescence, or but a very few bubbles of gas appear.

Experiment 41.—Dissolve in a similar way a small piece of 'caustic potash,' or potassium hydrate, and test it in the same way.

The two bodies just experimented with are often called 'the fixed alkalies,' or 'bases,' the latter term being generally applied to bodies which possess characters *opposed* to those of an acid. The formulæ of the two bases are the following—

NaOH . Sodium hydrate, or caustic soda.
KOH . Potassium hydrate, or caustic potash.

Opposed as acids and bases are in characters they can easily *neutralise* one another.

Experiment 42.—Take a piece of caustic soda

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about the size of a bean, dissolve it in about 30 c. cs. of water. Pour the liquid into an evaporating basin, *b*, fig. 34, and throw into the liquid a strip of blue litmus paper. Now add, drop by drop, colourless hydrochloric acid, stirring the liquid in the basin after each addition until the litmus paper begins to assume a reddish colour. If we now taste the solution it has a *salt taste*, the action of it on litmus paper is neither acid nor alkaline, and the solution is said to be *neutral*; the acid character of the hydrochloric acid has been exactly counter-balanced by the alkaline
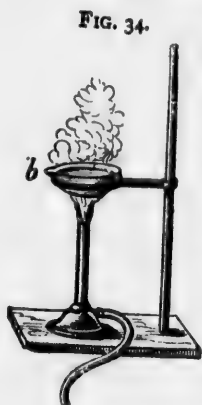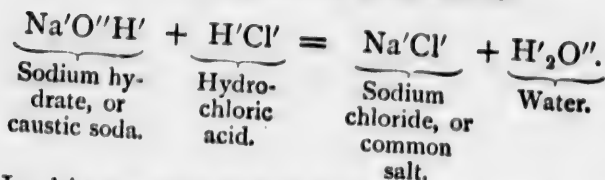
FIG. 34.

property of the caustic soda, and a *salt* is the product. If now we place the basin on the ring of the retort stand and apply heat, as shown in fig. 34, the solution soon boils, and the water is gradually converted into steam or vapour, and is driven off, or *evaporated*. When the liquid has been thus reduced to a very small bulk, little granular crystals separate. Pour off the liquid and allow the crystals to dry. They will then be found to possess the familiar characters of *common salt.* Therefore that body is produced when we neutralise hydrochloric acid by caustic soda. The formula of common salt is NaCl.
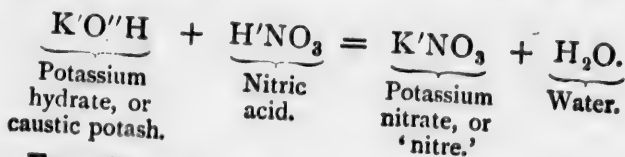
The following equation expresses the change :[1]—

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[1] If 'bread soda' instead of caustic soda be treated with hydrochloric, or other soluble acid, a gas—carbon dioxide, or 'Carbonic acid'— is evolved, as in Experiments 37, 38, and 39,
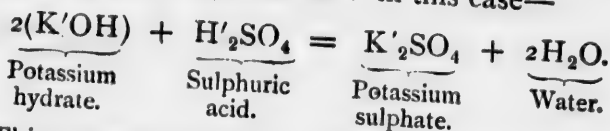
$$\underbrace{Na'O''H'}_{\substack{\text{Sodium hy-}\\\text{drate, or}\\\text{caustic soda.}}} + \underbrace{H'Cl'}_{\substack{\text{Hydro-}\\\text{chloric}\\\text{acid.}}} = \underbrace{Na'Cl'}_{\substack{\text{Sodium}\\\text{chloride, or}\\\text{common}\\\text{salt.}}} + \underbrace{H'_2O''}_{\text{Water.}}$$

In this case the H and Na change places, and we may regard this as equivalent to a replacement of the atom of H in HCl by the atom of monad Na.
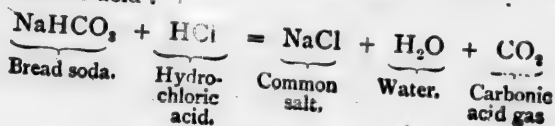
Experiment 43.—A precisely similar experiment may be made with caustic potash and nitric acid. In this case the salt crystallised from the neutral solution is common nitre.

$$\underbrace{K'O''H}_{\substack{\text{Potassium}\\\text{hydrate, or}\\\text{caustic potash.}}} + \underbrace{H'NO_3}_{\substack{\text{Nitric}\\\text{acid.}}} = \underbrace{K'NO_3}_{\substack{\text{Potassium}\\\text{nitrate, or}\\\text{'nitre.'}}} + \underbrace{H_2O}_{\text{Water.}}$$

Experiment 44.—Again, take some caustic potash and neutralise it with sulphuric acid, previously diluted with five or six times its volume of water. Evaporate the solution and hard crystals of the salt potassium sulphate, K_2SO_4, separate out : in this case—

$$\underbrace{2(K'OH)}_{\substack{\text{Potassium}\\\text{hydrate.}}} + \underbrace{H'_2SO_4}_{\substack{\text{Sulphuric}\\\text{acid.}}} = \underbrace{K'_2SO_4}_{\substack{\text{Potassium}\\\text{sulphate.}}} + \underbrace{2H_2O}_{\text{Water.}}$$

This equation states the fact that one molecule of sulphuric acid requires for neutralisation twice as

otherwise the same products are obtained. Thus, in the case of hydrochloric acid :

$$\underbrace{NaHCO_3}_{\text{Bread soda.}} + \underbrace{HCl}_{\substack{\text{Hydro-}\\\text{chloric}\\\text{acid.}}} = \underbrace{NaCl}_{\substack{\text{Common}\\\text{salt.}}} + \underbrace{H_2O}_{\text{Water.}} + \underbrace{CO_2}_{\substack{\text{Carbonic}\\\text{acid gas}}}$$

G 2

much (*i.e.*, two molecules) caustic potash as the molecule of nitric acid did. The reason for this is that the molecule of sulphuric acid contains *two* atoms of H, and, as we have already seen, each atom of H requires an atom of monad metal such as K to replace it ∴ two molecules of KOH were required, because the necessary number of atoms of K could not be obtained in any less quantity.

But, as we shall find later on, it is possible to displace only half the hydrogen by K in such an acid as sulphuric and to form an *acid salt*, $KHSO_4$, or acid potassium sulphate—a body which still contains hydrogen capable of replacement by a metal. The compound, K_2SO_4, is the neutral or 'normal' salt.[1]

Although it is not desirable to go much further in this direction at present, we can evidently draw the following conclusions from the foregoing experiments and statements.

1st. That acids do not necessarily contain oxygen, else the undoubted acid HCl could not belong to that class of bodies.

2nd. That the acids used contain H replaceable by a metal, with the production of a salt. This is true of *all* acids.

3rd. That all acids do not contain the same number of atoms of replaceable H within their molecules.

Those acids containing *one* atom of replaceable H,

[1] A group of bodies termed 'double salts' is known; common *alum* is a good example of such a salt, for in it we have united two normal salts, viz., potassium sulphate and aluminium sulphate. The formula of anhydrous alum may be thus written— $K_2SO_4, Al_2(SO_4)_3$.

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or 'basic hydrogen,' as it is sometimes called, are termed *monobasic* acids, and those containing two atoms are termed *dibasic* acids. *Tribasic* and *tetrabasic* acids, likewise exist, containing respectively three and four atoms of basic hydrogen. Generally, monobasic acids are the only members of the class which do not form acid salts.

It may be added that we can recognise in all salts an electro-positive constituent—the metal or metallike body—and an electro-negative constituent, or *acid radicle.* When the latter is an element, such as chlorine in $NaCl$, it is a *simple radicle*; but if it consists of a group of two or more elements, such as NO_3 in KNO_3, or SO_4 in K_2SO_4, it is called a *compound radicle.*

CHAPTER IX.

FURTHER EXPERIMENTS WITH HYDROGEN.

HYDROGEN. *Symbol* $H' = 1$. 1 *Vol weighs* 1 *c.gr. Molecular weight* $= 2$.—This element, which was discovered by Cavendish in 1766, has already been experimented with, and we have found it to be a colourless, inodorous, and extremely light gas, which can burn in air, and then affords water as the sole product of its combustion. We have also proved that it forms $\frac{1}{9}$th of water by weight.
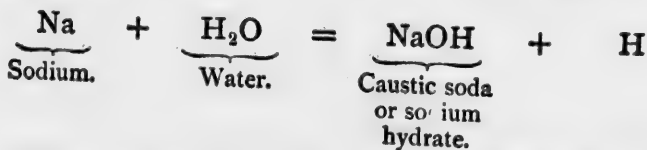
Water is the chief terrestrial storehouse of hydrogen, for it rarely occurs in the free state upon the earth, save in certain gases which issue from active volcanoes. It is a constituent of animal and vegetable tissues, and of *all true acids.*

The hydrogen can be liberated from *water*, as we have already seen (Experiment 22), by electrolysis, in which case the compound is resolved into its constituents

$$H_2O = 2H + O.$$
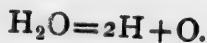
Experiment 45.—Hydrogen is also separated from water when we project a pellet of the metal sodium, the size of a pea, on some cold water contained in a dish. The water is decomposed with a hissing noise as the globule of metal rolls about on the surface,

and if a flame be brought near to it, the hydrogen gas evolved is ignited, and burns with a yellow flame, until the sodium disappears. If we do not ignite the gas, the metal also disappears, dissolving in the water.
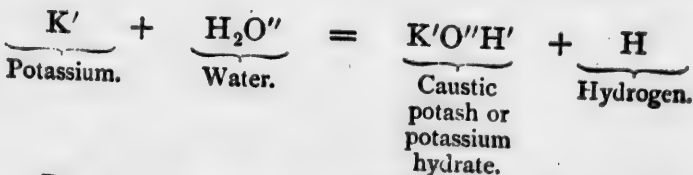
$$\underbrace{Na}_{\text{Sodium.}} + \underbrace{H_2O}_{\text{Water.}} = \underbrace{NaOH}_{\substack{\text{Caustic soda} \\ \text{or sodium} \\ \text{hydrate.}}} + H$$

The caustic soda can be recognised in the water by its property of turning reddened litmus paper blue. See Experiment 40.

In this case the monad metal replaces only *one* atom of H in the water molecule and a *metallic hydrate* is formed, or sodium water, *i.e.* water in which the hydrogen *rôle* is played in part by the Na.[1]

H'O''H' . . . . Water.
Na'O''H' . . . . Sodium hydrate.

Experiment 46.—If we substitute a pellet of the metal potassium for the sodium in the last experiment, the metal also dissolves and produces potassium hydrate.

$$\underbrace{K'}_{\text{Potassium.}} + \underbrace{H_2O''}_{\text{Water.}} = \underbrace{K'O''H'}_{\substack{\text{Caustic} \\ \text{potash or} \\ \text{potassium} \\ \text{hydrate.}}} + \underbrace{H}_{\text{Hydrogen.}}$$

But in this case the temperature of the evolved

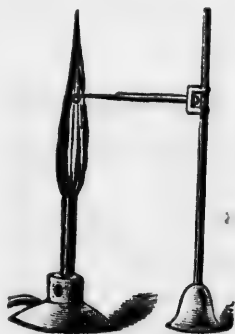[1] It is possible to displace the second atom of H in water by another atom of Na, but not in presence of much free water as in the experiment.

hydrogen is raised by the heat of chemical action to such a point that it takes fire in the air, and burns with a reddish violet flame: thus the metal seems to set fire to the water !

**Experiment 47.**—As we have already seen, the colour of the pure hydrogen flame is a very faint blue, but the yellow flame observed in Experiment 45 is due to the presence of a little sodium vapour, which communicates to the flame the characteristic tint observed. Any compound of sodium, such as common salt, NaCl, will also communicate a strong yellow tint to an otherwise colourless spirit or gas flame, if we introduce a little of the solid supported on a loop of platinum wire, as in fig. 35. This is therefore a *flame test* for sodium.

Fig. 35.

Similarly potassium and its compounds communicate an equally characteristic reddish violet colour to flame.
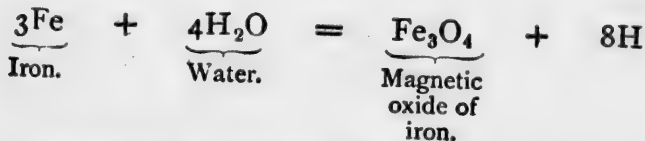
Experiment 48.—Hydrogen can also be displaced from water by the action of red hot iron on steam. Take an old gun barrel, fig. 36, and fill it to within a few centimeters of each end with bright iron turnings or borings ; then pass the tube through the little charcoal furnace *f*, and connect one end *b* by means of a cork and leaden tube *d* with the flask *c*, in which some water can be made to boil and afford a current of steam. Attach a cork *a* and gas delivery tube *e* of lead or glass to the other end, and let *e* dip under

the surface of the water in the pneumatic trough *f.* When the iron tube has been heated to full redness,

F̲ɪɢ̲. 36.
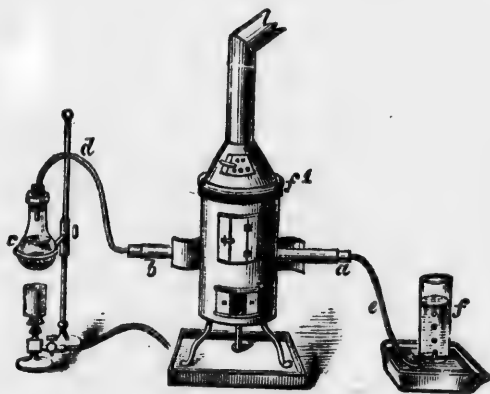
boil the water in *c* and pass in the steam.   Gas will issue from the delivery tube, but most of it is air at first, and may be allowed to escape ; a few tubes full are then collected, and may be tested as in Experiment 19.   The following equation represents the change.

$$\underbrace{3\text{Fe}}_{\text{Iron.}} \quad + \quad \underbrace{4\text{H}_2\text{O}}_{\text{Water.}} \quad = \quad \underbrace{\text{Fe}_3\text{O}_4}_{\substack{\text{Magnetic}\\\text{oxide of}\\\text{iron.}}} \quad + \quad 8\text{H}$$

In this case a metallic hydrate is not formed, but a *metallic oxide* is produced.   It has been found, by careful experiment, that three atoms of the iron, or 168 c. grs. (56×3), liberate eight atoms, *i.e.* 8 c. grs. of H by weight, and these data enable us to calculate the weight of H which can be evolved by any given

weight of iron (say 10 centigrams) from an excess of steam. Thus in the case supposed :—

$$168 : 10 \therefore 8 : \text{X} \quad (\text{X} = \cdot476 \text{ c. grs.}—Ans.).$$

Hydrogen can also be displaced from sulphuric acid by the action of magnesium, as in Experiment 17, and by iron or zinc, Experiment 19. Zinc is the metal most commonly used.

Experiment 49.—Fit up the apparatus as in Experiment 19. Having introduced the zinc, and filled the bottle one-third with water, replace the cork, and pour two or three cubic centimeters of acid down the thistle funnel. Hydrogen is soon evolved as before, and gas bubbles through the water in the trough. Allow a volume of gas, judged to be about equal to twice the capacity of the bottle, to escape, and then collect in jars for experiment, as before.

$$\underbrace{Zn''}_{\text{Zinc.}} + H'_2SO_4 = \underbrace{Zn''SO_4}_{\text{Zinc sulphate.}} + 2H$$
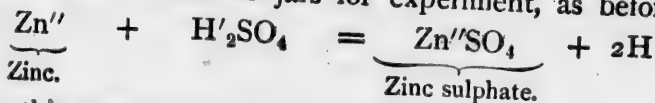
In this case, the single atom of diad zinc displaces the two atoms of monad H from the acid, and forms zinc sulphate which remains in solution.

Experiment 50.—When all evolution of gas has ceased, remove the cork, and pour the contents of the bottle on a filter, supported by a funnel as in fig. 37,[1] any undissolved zinc, and particles of carbon,

[1] A filter is thus made. Cut a circular piece of white bibulous paper about a decimeter in diameter, double this so as to form a semicircle, and double again so as to form a quadrant, now convert this into a paper cone with *three* folds of the paper on one side, and one fold or thickness on the other. Place this, point downwards, in the funnel, as shown, and moisten with a little water.

lead, and other impurities not dissolved by the diluted acid are left behind on the filter, while a clear liquid passes through, and the latter when evaporated (as in Experiment 42), until a pellicle or crust begins to form on the surface of the solution, deposits fine needle-shaped crystals of the salt, zinc sulphate—a body having the composition $ZnSO_4, 7H_2O$. The water included in the formula is termed 'water of crystallisation,' as its presence is essential to the existence of the

FIG. 37.

crystals as such, but not to that of the compound zinc sulphate, as almost every trace of the water can be driven off in the form of steam when the crystals are carefully heated to a temperature of 260° C.
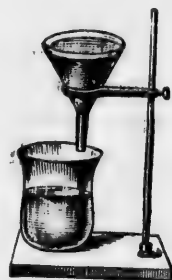
Experiment 51.—After repeating former experiments take a gas jar standing over water in the trough, half fill with hydrogen and the remainder with air, remove and quickly apply a flame, and an explosion takes place. If pure oxygen be used instead of atmospheric air, the tube should be two-thirds filled with hydrogen and the rest with oxygen. In the latter case the explosion is more violent, and it is well to wrap the jar in cloth before applying the flame.

Hydrogen gas, when inhaled into the lungs of animals, causes death by excluding air.

Hydrogen forms two compounds with oxygen—one, water, H_2O, whose composition we have already determined; and a body termed peroxide of hydrogen,

or oxygenated water, H_2O_2, whose preparation and properties will be referred to later on.

Experiment 52.—The ease with which hydrogen combines with oxygen renders it a useful 'reducing' or *deoxidising* agent, especially when heated. Take a tube, about 1 centimeter in diameter, and 20 centimeters long. Place midway in it, at a, fig. 38, a small quantity of black oxide of copper, CuO, and connect the tube as shown with the hydrogen bottle b, taking care to

FIG. 38.
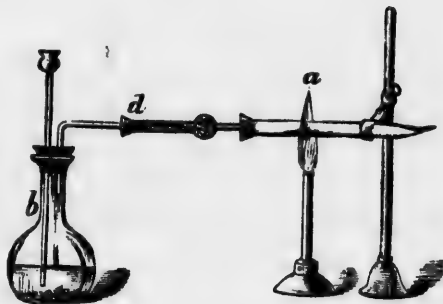
interpose the drying tube d filled with calcium chloride, so as to remove moisture from the gas. Generate hydrogen as usual and keep up a steady current through the apparatus. When all air has been expelled, but not till then, apply heat to the tube so as to raise the temperature of the copper oxide at a; the latter soon begins to glow and steam issues freely from the end of the tube. The lamp may be removed, and when the glowing ceases the tube is seen to contain a red body, easily identified as metallic copper. The change is expressed by the equation—

$$\underbrace{Cu''O''}_{\substack{\text{Copper} \\ \text{oxide.}}} + 2H = \underbrace{Cu}_{\substack{\text{Metallic} \\ \text{copper.}}} + H_2O.$$
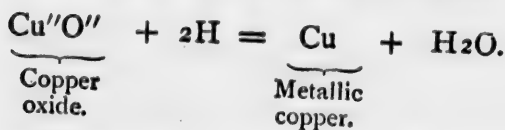
This reaction was employed by MM. Dumas and Boussingault in order to determine with extreme precision the composition of water by weight. They heated to redness a carefully weighed quantity of pure copper oxide in a current of perfectly pure and dry hydrogen gas, and collected and weighed the water produced.[1] In one of their experiments the cupric oxide lost 59·789 grams of oxygen, and the water produced weighed 67,282 grams. The composition of this weight of water is, therefore—

Hydrogen	7·493
Oxygen	59·789
	67·282

Calculate the *percentage* composition of water and deduce the formula from these data by the method given at page 70.

Experiment 53.—Substitute for the copper oxide in Experiment 52 some iron rust in fine powder. The red rust—consisting chiefly of a sesquioxide[2] of iron—then becomes greyish black when heated to redness in hydrogen, and water is produced. The black

---

[1] We have already (Experiment 21) made a similar experiment by another method, *viz.*, by the combination in air of a weighed quantity of hydrogen gas, the weight of water produced being collected and weighed.

[2] From *sesqui*—one and a half, for the ratio of Fe to O is 1 to $1\frac{1}{2}$; but since an atom is indivisible, the simplest expression for the oxide is Fe_2O_3.

body left in the tube chiefly consists of metallic iron in a very fine state of division, in which condition the metal easily takes fire, if the warm powder be poured out through the air.[1] In this condition the metal is said to be *pyrophoric.*

$$Fe_2O_3 + 6H = 2Fe + 3H_2O.$$
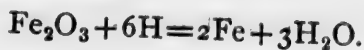
Thus prepared from pure oxide, the metal constitutes the *Fer réduit*, or *Ferrum redactum* of the British Pharmacopœia.

Hydrogen gas is absorbed by water in very small proportions, 100 cubic centimeters of the latter dissolve only 1·93 c. cs.   But some solid metals absorb hydrogen, notably the metals platinum[2] and palladium. The latter take up no less than 370 volumes of the gas at ordinary temperatures.

Hydrogen gas has been recently condensed by M. Pictet of Geneva to a liquid, exhibiting steel-blue *metallic* lustre, under the enormous pressure of 650 atmospheres, and at a temperature of 140° C. below zero : the gas is, therefore, to be regarded as the vapour of a highly volatile *metal.*

[1] The same weight of iron in the form of wire would but slowly rust or oxidise when exposed to the air; the above experiment therefore well illustrates the effect of a fine state of division in determining rapid chemical changes.

[2] For a description of the Döbereiner lamp see Platinum.

CHAPTER X.

EXPERIMENTAL DETERMINATION OF THE VOLUME OCCUPIED BY ONE CENTIGRAM OF HYDROGEN.

WE have already learned from Experiment 18 that 1 centigram weight of hydrogen gas is evolved from acidulated water during the solution of 12·2 c. grs. of pure metallic magnesium; we, therefore, know how to get our unit weight of hydrogen. In the experiment cited we allowed the gas to escape: we shall now collect the gas and measure it.

Experiment 54.—Obtain a tube about 40 c. ms. long and ·2 c. ms. internal diameter, graduated into 130 cubic centimeter divisions, *a*, fig. 39. Dilute 50 c. cs. of oil of vitriol with about a liter of water in a jug, and throw into the liquid a few scraps of metallic zinc. Hydrogen will be developed and the liquid will have nearly or quite saturated itself with the gas in a few minutes. Next pour some of the diluted acid into a tall narrow beaker *b*, and, having filled the graduated tube

FIG. 39.
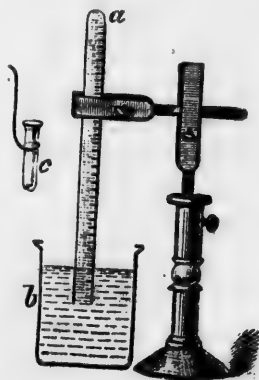
completely with the same liquid, invert it in the acid in the beaker and support it as shown.

Now weigh out 12'2 c. grs. of pure and clean metallic magnesium—the weight of the metal that we know will liberate 1 c. gr. of hydrogen—and place it in the bottom of a narrow test tube, *c*, to the middle of which a wire is attached to serve as a handle. The tube is then filled with water and plunged under the surface of the acid in *b*, and the upturned mouth of the test tube *rapidly* brought under the mouth of the graduated tube, and even passed up into the latter. Very soon the acid liquid displaces the water in the test tube and the metal is attacked; the hydrogen gas evolved passes into the inverted tube and there collects. When the last trace of magnesium disappears the action is at an end, and we have confined in the tube the volume of pure hydrogen gas that weighs 1 centigram. Now depress the tube in the acidulated water until the liquid within and without the tube stands at the same level, and read off the volume of the enclosed gas. Immediately afterwards read the *temperature* as indicated by a thermometer in the neighbourhood of the apparatus, and the *pressure* as indicated by a barometer.

A more precise experiment can be made with the apparatus, fig. 40. The stand A supports a tall glass cylinder, B. Through the large india-rubber cork which closes the lower opening of the cylinder the U tube *c* is passed, great care being taken to avoid breaking the small T connector *c*. The outer limb of the U tube is provided with a glass tap T. The limb within the tall glass cylinder is sufficiently wide

to contain 150 cubic centimeters in the expanded portion, which, in our apparatus, measures sixty centimeters in length. The graduation cannot be conveniently carried beyond fifths of a cubic centimeter. At the point shown an india-rubber tube g is attached, which can be closed at will either by a good clip or by a stopper of glass rod. The glass side tube c serves to connect the measuring apparatus, filled to 0 with water, with the generating vessel D, which is a long and wide glass tube placed within the cylinder. The glass T tube E is connected by means of rubber tubing with c, while one limb passes through the india-rubber cork of D, and the other is connected by another

Fig. 40.
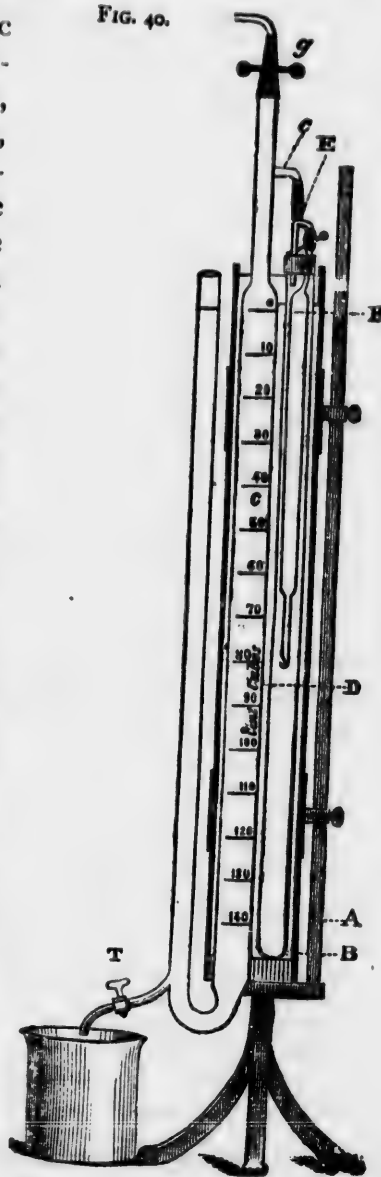
piece of rubber tubing with a fine tube of the long pipette F (of about 20 c.cs. capacity), which projects through the cork. This connection must be sufficiently long to admit of the clip being applied as shown.

The large glass cylinder B is filled with water, in order to maintain a steady temperature, the value of which can be known by means of a thermometer immersed in the water.

A determination is made with this apparatus in the following way:—Having disconnected the T tube E from c and removed the clip, the tube D is taken out of the water of the cylinder, the cork carrying the pipette, &c., withdrawn, and then 12·2 c. grs. of magnesium introduced into the tube D. Before replacing the cork the pipette F is filled with diluted sulphuric acid by suction at E, while the small glass tube opening on the under side of the cork is closed by a finger: the clip is then applied. The exterior of the pipette is now washed with a little water, and the cork, with the apparatus attached, is then replaced in position; the tube D again immersed in the water of the large cylinder, and the joint between E and c securely made. Before making the connection the water in the graduated tube should stand at the zero of the scale, but after securing the joint the pressure within the apparatus is usually greater than that without. As the air in the tube D cools down to the temperature of the surrounding water, contraction takes place; but should the water not return to the zero, equilibrium is at once restored by opening the fine india-rubber tube g for a few

seconds, and then closing in such a manner as to prevent any possible escape of gas.

The acid is brought in contact with the magnesium by removing the clip from the india-rubber tube connected with the pipette; the reagent then falls upon the metal at the bottom of the tube D. Hydrogen is evolved and displaces water from c, the liquid being maintained at the same level in both limbs of the U tube by allowing the water displaced to run off by means of the tap T. When the evolution of gas has ceased, the water level is adjusted by means of the tap, and the volume of gas produced in the reaction then read off on the graduated tube; the temperature of the water in the cylinder B is then ascertained, as well as the height of the barometer at the time. From the data thus obtained, the volume of dry hydrogen at 0° C. and 760 mm. can be easily calculated.

A student obtained, as the result of an experiment made in this way, 121 cubic centimeters of pure but moist hydrogen, measured at 16° C. and 755 millimeters pressure, during the solution of 12·2 c. grs.[1] of magnesium in acidulated water.

So far for our experiment : we now have to find the volume this gas would occupy if dry and measured at 0° C. and 760 millimeters—the ' standard temperature and pressure ' to which all gaseous volumes are corrected, for reasons that will presently appear

The corrections are three in number—namely: for *tension of aqueous vapour*, for *pressure*, and for *tem-*

[1] The 2 milligrams in excess represent the known proportion of impurity in the sample of metal.

perature, and we shall deal with each in some detail in order to illustrate the method of solving such problems.

1. *Correction for tension of aqueous vapour.*[1]—We find from the annexed table of tensions for different temperatures that at 16° C. the pressure exerted by vapour of water =13·5 mm., that is to say, the pressure exerted by the aqueous vapour within the tube tended to balance the atmospheric pressure to the extent of a column of mercury of 13·5 millimeters in height ; therefore the actual pressure under which we measured the confined gas was

$$755 - 13\cdot5 = 741\cdot5 \text{ millimeters of mercury.}$$

TENSIONS OF AQUEOUS VAPOUR.

Degrees Centigrade			Tensions in millimeters of mercury	Degrees Centigrade			Tensions in millimeters of mercury
0	•	•	• 4·60	19	•	•	• 16·34
5	•	•	• 6·53	20	•	•	• 17·39
10	•	•	• 9·16	30	•	•	• 31·54
11	•	•	• 9·79	40	•	•	• 54·90
12	•	•	• 10·45	50	•	•	• 91·90
13	•	•	• 11·16	60	•	•	• 148·70
14	•	•	• 11·90	70	•	•	• 233·00
15	•	•	• 12·69	80	•	•	• 354·60
16	•	•	• 13·53	90	•	•	• 525·40
17	•	•	• 14·42	100	•	•	• 760·00
18	•	•	• 15·35				

2. *Correction for pressure.*—We learned from Experiment 28 that when a confined mass of gas was

[1] The student must refer to a work on Physics for full details of corrections of gases.

compressed, its volume or bulk *diminished with increase of pressure*, and conversely, *increased in volume as the pressure diminished.* Thus, if the pressure on a given mass of gas be doubled, the volume is reduced to *one-half*, and if trebled, to *one-third*, and so on. When the original pressure is restored the gas returns to its original volume. If now we *reduce* the pressure to one-half, the volume of gas is *doubled*; if to one-third, the volume is *trebled*, and so on. These facts find expression in the law of Boyle or Mariotte : ' *The volume which a gas occupies is inversely proportional to the pressure to which it is subjected.*' Now 741·5 mm. being a lower pressure than the standard 760 mm., our gas would occupy a less volume at the greater pressure ; how much less we find thus—

$$760 : 741\text{·}5 \therefore 121 : \times \ (\times = 118\text{·}5 \text{ c.cs.}).$$

3. *Correction for temperature.*—Experiment 28 also showed us that gases expand equally when heated, and contract when cooled. If we begin with a given volume of gas at the temperature of melting ice, *i.e.* 0° C., and measure the gas as we raise its temperature at a definite rate, we find that for each rise in temperature by 1° C. the gas expands $\frac{1}{273}$rd of its volume at 0° C. That is to say, 273 c.cs. at 0° C. expand to 274 c.cs. if the temperature be raised to 1° C. ; or to 280 c.cs. if heated to 7° C. ; or to 289 c.cs. if heated to 16° C. ; the pressure throughout being constant. Similarly, 289 c. cs., cooled to 0° C. contract to 273 c. cs. Hence we can easily find the volume that 118·54 c.cs of gas at 16° C. would occupy if cooled to 0° C. ; thus—

$$289 : 273 \therefore 118\text{·}5 : \times \ (\times = 111\text{·}9 \text{ c.cs.}).$$

The final result is that 1 centigram of pure dry hydrogen, when measured at 0° C. and 760 mm. pressure, occupies as nearly as possible 112 c.cs. As we have already adopted the centigram as our unit of weight, we may conveniently take the bulk of 1 c.gr. of hydrogen, measured under standard conditions, as our unit of volume, and call it briefly a *vol.* Thus when we speak of 1 *vol* of any gas, we mean 112 c.cs. of it measured at 0° C. and 760 mm. [1]

The *vol* as thus defined is a small and convenient quantity of a gas, which is well within the capacity of the ordinary measuring vessels used in laboratories; moreover it possesses the great advantage over the liter as a unit of gaseous volumes, that its weight in hydrogen is identical with the atomic weight of that body in centigrams; consequently a *vol* of any other elementary gas weighs the number of centigrams indicated by the atomic weight of the element. Thus—

Name of gas	Atomic weight	Weight in centigrams of 1 *vol* (at 0°C. and 760 mm.) or 112 c. cs.
Hydrogen • • •	1.0	1.0 c. gr.
Oxygen . • • •	16.0	16.0 ,,
Nitrogen • • •	14.0	14 0 ,,
Chlorine • • •	35.5	35.5 ,,

[1] A number of *vol* tubes may be prepared by cutting a good cylindrical glass tube 4.2 centimeters diameter into lengths of 7.8 centimeters, one end of each tube is then closed by a glass plate which is cemented on. Each tube or jar should hold 112 c. cs. of water. We have a number of these jars prepared and filled with different coloured wool, in order to illustrate the volume relations of elementary and compound gases.

Hence in order to find the weight of a given bulk of gas, for instance, of 900 c.cs. of hydrogen at standard temperature and pressure, it is merely necessary to proceed as under :—

$$112 : 900 \therefore 1 : \maltese (\maltese = 8{\cdot}03 \text{ c.grs.}).$$

But if the gas were oxygen—

$$112 : 900 \therefore 16 : \maltese (\maltese = 128{\cdot}57 \text{ c.grs.})$$

Generally— $$\maltese = \frac{n \times \text{at. wt.}}{112}$$

Since the *vol* of hydrogen represents the semi-molecule of that element, the molecular weight being 2 as we have already seen (see page 52), the *vol* also represents the semi-molecule of any compound gas— water gas, for example—consequently the weight of one *vol* of a compound gas is half the molecular weight in centigrams. Thus—

Name of gas	Molecular Formula	Molecular weight	Weight in centigrams of one *vol* (at 0°C. and 760) or 112 c. cs.
Hydrogen	H_2	2	1 c. gr.
Water gas	H_2O	18	9 ,,
Hydrochloric acid gas	HCl	36.5	18.25 ,,
Ammonia	NH_3	17	8.5 ,,
Marsh gas	CH_4	16	8 ,,
Carbon dioxide	CO_2	44	22 ,,
Carbon monoxide	CO	28	14 ,,

The numbers in the fourth column are identical with the specific gravities of the gases referred to hydrogen as the standard. *In order to find the weight*

in centigrams of a given bulk of a compound gas—for instance, of 1200 c. cs. ($=1\cdot2$ liters) of ammonia gas at standard temperature and pressure—we say—

$$112 : 1200 \therefore 8\cdot5 : \maltese \quad (\maltese = 91 \text{ c. grs.}).$$

If the gas were hydrochloric acid gas—

$$112 : 1200 \therefore 18\cdot25 : \maltese \quad (\maltese = 195\cdot5 \text{ c. grs.}).$$

Generally—

$$\maltese = \frac{n \times \text{sp. gr.}}{112}$$

when $n =$ the number given in cubic centimeters of dry gas at $0°$ C. and 760 mm.

Instead of the *vol*, we may use the liter as our unit of volume. The weight of a liter of pure dry hydrogen at $0°$C. and 760 mm. is $\cdot08936$ (this weight is called by Dr. Hofmann a *crith*). A liter of oxygen weighs 16 criths, of chlorine $35\cdot5$ criths, of nitrogen 14 criths, &c. A liter of water-gas weighs 9 criths, of ammonia $8\cdot5$ criths, of hydrochloric acid gas $18\cdot25$ criths, &c.

We have already learned from Experiment 29 that the specific gravity of the compound water gas is half its molecular weight; and the above table tells us the same thing for other compound gases. If then we have presented to us a gas of unknown composition, *we can determine its molecular weight* by first taking its specific gravity, as in Experiment 27, and that value, when doubled, should give the molecular weight of the compound. Thus, ammonia gas has the specific gravity $8\cdot5$, its molecular weight is therefore $8\cdot5 \times 2 = 17$.

Hydrochloric acid gas has the specific gravity $18\cdot25$; the molecular weight of the compound is therefore $18\cdot25 \times 2 = 36\cdot5$.

There are a few exceptions to this important rule, which will be noticed in the proper place.

Experiment 55.—Take a U tube of the form shown in fig. 41, with limbs 60 centimeters long. Let one limb be hermetically sealed at the top and the other open. A stopcock is provided near to the bend of the open limb. Now fill both limbs completely with mercury so as to expel all air, then insert the cork *i*, through which passes the end of a small tube open at both ends, and filled with fragments of calcium chloride. Now open the stopcock *s*, and allow about half the mercury to flow out, while *dry* air enters through the drying tube *c*. Next transfer this dry air to the closed limb by inclining the tube sufficiently. Then bring the mercury in both limbs to the same level by drawing off some through the stopcock. Should the volume of air in the closed limb be less than half the tube full, after levelling, transfer sufficient to make up the desired volume, and level again, but this time by removing the cork and pouring into the open limb sufficient mercury. The cork and tube *c* need not be replaced.

FIG. 41.
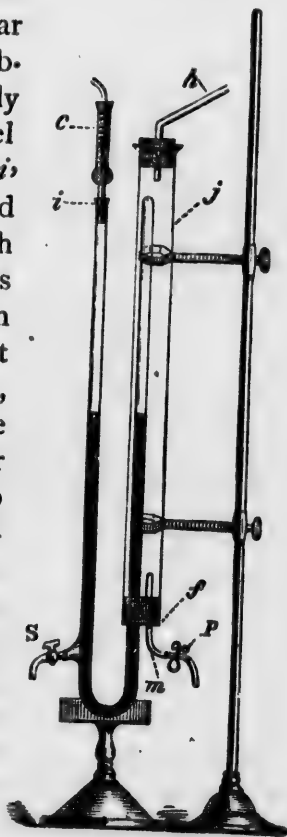
We have now a confined mass of dry air in the closed limb. Place over this tube a glass jacket *j*, which is stopped below by the cork *f*, through which the closed limb passes, and the small side tube *m*. Fill up the space between the exterior of the U tube and the jacket with pounded ice. This will soon cool down the air in the tube, and the gas will contract in volume. When no further contraction takes place, again adjust the level of the mercury in the two limbs, and mark off as accurately as possible in the outer tube the position of the mercury in the closed limb. This marks on the tube the volume occupied by the dry air at the temperature of melting ice, *i.e.* at 0° C.

Now pour tepid water into the jacket *j*; this will melt the remaining ice, and the water will flow off through the side tube *m*, which is opened or closed at pleasure by the pinchcock or clip *p*, that compresses a piece of india-rubber tubing attached to *m*. When the ice has melted, and the water been drawn off, remove the pinchcock *p*, and connect the tube *h*, by means of vulcanised tubing, with a flask from which a good current of steam can be obtained by rapidly boiling water contained in it; the steam rushes through the jacket and the excess may be allowed to pass off into the air through the tube *m*. As the air n the closed limb becomes heated it expands until it has acquired the temperature of the steam. When it ceases to expand, adjust the level of the mercury as before, and mark on the tube the volume occupied by the dry air at the particular temperature.

Now divide the interval between the two points

marked into 100 equal parts, by transferring the length to cardboard, and plotting off the intervals. With the scale thus obtained, measure the distance from the position occupied by the mercury when the gas was cooled to the temperature of melting ice, to the sealed top of the tube, and it will be found that the end of the tube is reached, as nearly as possible, at 273 DIVISIONS of the scale. This point is termed the *absolute zero,* for it is evident that the contraction of the gas could not go beyond this point, even if it contracted with regularity nearly to its limit. If then we represent the top of the tube as absolute zero, or 00°, the enclosed air at the temperature of melting ice will occupy the position 273°, and that of free steam the position of 373°, on such a scale of absolute temperature ; hence the 'law' enunciated by Charles, that *the volume of a given mass of gas, under constant pressure, is directly as its* ABSOLUTE *temperature, i.e.,* as its temperature measured from absolute zero. This is 273 + *t, t* being the number of degrees above the freezing-point on the scale of the centigrade thermometer.

CHAPTER XI.

EXPERIMENTS WITH OXYGEN AND OZONE.

OXYGEN—*Symbol,* $O''=16$. 1 *Vol weighs* 16 *c. grs. Molecular weight*$=32$.—We have already proved conclusively that oxygen is not only a constituent of water, and that it forms $\frac{8}{9}$ths of that body by weight, but also that it is present in atmospheric air. Later on, we shall find that it is met with in most of the chemical compounds of which the solid crust of our globe is composed, but in the air alone do we find the element in a free state (*i. e.* not in chemical combination), though mixed with four times its volume of another gas called nitrogen. We do not possess a convenient process for the direct separation of oxygen from air, hence we always prepare it from one or other of its compounds. Oxygen can be prepared from water by electrolysis, as already described, Experiment 22,

$$H_2O = 2H + O,$$
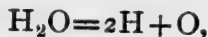
or more conveniently by heating certain bodies which easily yield oxygen—for example—mercuric oxide, or the salt called potassium chlorate.

Experiment 56.—Take a tube of hard glass, *t,* fig. 42, closed at one end, and fitted with a cork and delivery tube as shown. Place in the tube about 200

c. grs. of red oxide of mercury, the 'red precipitate' of the druggists. Heat gently at first, and then increase the temperature. Gas will soon escape from the delivery tube and bubble through the water in the pneumatic trough. After expulsion of the air, the gas collected is found to have the property of rekindling a match with a glowing tip, and is oxygen ; at the same time it will be observed that bright metallic globules con-

Fig. 42.

dense on the sides of the tube *t*, and, if the heat be continued long enough, the pure mercuric oxide is wholly resolved into oxygen gas, and globules of the liquid metal mercury or quicksilver. Thus :—

$$\underbrace{Hg'' O''}_{\text{Mercuric oxide.}} = \underbrace{Hg}_{\text{Mercury.}} + \underbrace{O}_{\text{Oxygen.}}\text{[1]}$$
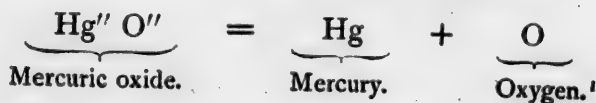
This process is not an advantageous one for the preparation of oxygen in quantity, but it possesses special interest, since it is the method by which the element was first prepared by its discoverer, Dr. Priestley, in 1774.

Oxygen can also be obtained by heating manga-

[1] Therefore 216 c. grs. of HgO afford 16 c. grs. of O, the weight of one *vol* at 0°C. and 760 mm.

nese dioxide, in which case the following decomposition takes place—

$$3\,Mn\,O_2 = Mn_3\,O_4 + 2\,O.$$

Barium dioxide and other similar bodies also afford the gas, and the processes will be described under the respective compounds; but the most convenient method is the following :—

Experiment 57.—Fit a flask—a clean Florence oil flask answers well—with a cork and delivery tube

FIG. 43.
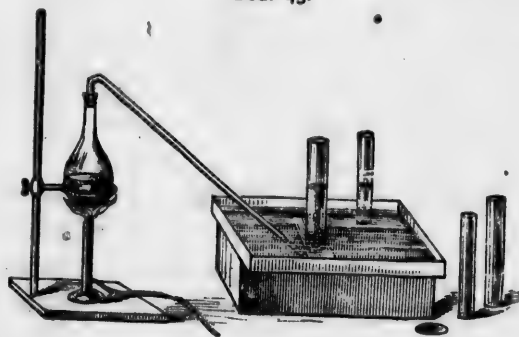
as shown in fig. 43. Break up some crystals of the salt potassium chlorate ($KClO_3$) in a mortar, then mix with about one-third of its weight of black oxide of manganese (manganese dioxide), and pour the mixture into the flask, but reserve a small portion and heat the latter strongly in a test tube before applying heat to the contents of the flask. If no violent action takes place when the small quantity is heated, the manganese used may be considered free from any dangerous impurity, such as charcoal, soot, or lamp black, with which it is sometimes accidentally mixed

or even adulterated ;[1] then heat the flask. After expulsion of the air, the gas can be collected in several jars or in wide-mouthed bottles over the water in the pneumatic trough, as 100 c.cs. of water dissolve but 2·989 c.cs. of gas at 15° C. If it be desired to store a quantity of the gas for a number of experiments, the gas-holder shown in section, fig. 44, is to be employed.
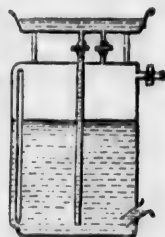
The heat resolves the potassium chlorate into oxygen gas and potassium chloride, which latter remains in the flask at the end of the operation along with the black oxide of manganese ; for the latter body is not known to undergo any chemical change during the operation, though its presence undoubtedly enables the oxygen to separate at a lower temperature than it otherwise would. The following equation represents the ultimate change :—

$$K' \, Cl' \, O''_3 \quad = \quad K' \, Cl' \quad + \quad 3\,O$$

$$\underbrace{}_{\substack{\text{Potassium} \\ \text{chlorate.}}} \qquad \underbrace{}_{\substack{\text{Potassium} \\ \text{chloride.}}}$$
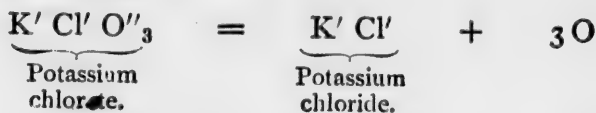
The potassium chloride left is easily soluble in water, whereas the black oxide of manganese is insoluble ; we can take advantage of these facts in order to separate the two bodies. Add some warm water to the contents of the flask, allow the mixture to stand for half an hour or so, and then throw the dirty black mixture on a paper filter. The clear liquid passes

[1] Several fatal accidents have resulted from such admixture.

through and is collected in a beaker, while the solid particles of the insoluble manganese dioxide are retained by the filter and thus separated. When all the liquid has passed through the filter, place the dish on a ring of a retort stand, and evaporate (as in Experiment 50) until all the water is removed, and a white saline body remains. This is the potassium chloride.

With the aid of the equation just given we can easily calculate the weight and the volume of pure oxygen gas, at 0° C. and 760 mm. that a given weight, say 100 c.grs., of the pure potassium chlorate can afford by complete decomposition. The molecular weight of $K Cl O_3$ is 122·6, and this is found by the general method of adding together the weights of the constituent atoms, *i.e.*, K=39·1, Cl=35·5, 3 O=48 (=16 × 3). Since all the oxygen is evolved when the salt is strongly heated for a sufficient time, it follows that 122·6 c.grs. of $K Cl O_3$ can afford 48 c.grs. of O. Hence the weight of gas 100 c.grs. can yield is—

$$122·6 : 100 \therefore 48 . \text{ } ℵ \text{ } (ℵ = 39·15 \text{ c.grs. } Ans.).$$

We have now to find the volume:—16 c.grs. of oxygen at 0° C. and 760 mm. measure 1 *vol* (=112 c.cs.); now

$$16 : 39·15 \therefore 112 : ℵ \text{ } (ℵ = 274 \text{ c.cs. } Ans.).$$

The general answer therefore is—100 c.grs. of pure potassium chlorate afford 39·15 c.grs. of oxygen gas, which occupies the volume of 274 c.cs. at 0° C. and 760 mm. The same method is employed in all similar calculations, as for instance in the calculation of the

volume of oxygen that can be collected on heating a given weight of red oxide of mercury.[1]

We already know that oxygen gas is colourless, inodorous, and a powerful supporter of combustion. With the jars or bottles of gas already collected make the following experiments :—

Experiment 58.—Take a small lump of charcoal and twist a piece of copper wire round it. Hold the charcoal in the spirit or gas flame until it is kindled, and then plunge it into a jar of oxygen. The charcoal burns energetically in the pure gas, emitting much light and heat. In this and similar experiments it is well to provide a cover for the jar of cardboard, through a hole in which the wire passes. When the combustion is at an end remove the charcoal and pour into the jar some clear *lime water*—note that the latter becomes milky when the mouth of the jar is closed with the hand and the contents shaken. The reason is that the product of the combustion of charcoal (carbon) in oxygen is a gas called carbon dioxide, this forms insoluble *chalk*, or calcium carbonate, when it meets with lime water (solution of calcium hydrate); the latter is, therefore, a *test* for the gas.[2] These reactions are thus represented—

$$\underbrace{C}_{\text{Carbon.}} + 2O = \underbrace{CO_2}_{\substack{\text{Carbon} \\ \text{dioxide.}}}$$
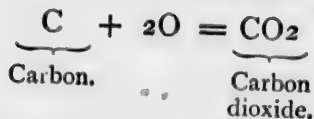
[1] The method is reversed when we desire to calculate the weight of a body required to afford a given volume of gas.

[2] If lime water be shaken in a jar of pure oxygen it does not become turbid.

I

Then—

$$CO_2 + \underbrace{Ca''(OH)'_2}_{\text{Calcium hydrate.}} = \underbrace{Ca''CO_3}_{\text{Calcium carbonate.}} + H_2O.$$
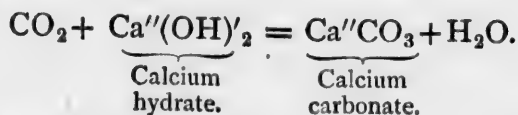
The chalk is the calcium salt of an acid H_2CO_3 formed by the action of water on the gas CO_2.

Experiment 59. — Place a small quantity of sulphur in the iron spoon, fig. 45, and kindle it, when feebly burning plunge it into a jar of oxygen. The sulphur burns with a beautiful blue flame, and a gas—sulphur dioxide—havi. g a suffocating odour, is the product. Remove the spoon, pour some water into the jar, close the mouth with the hand and shake. Now test the water in the jar with some blue litmus paper. It will be found to *redden* the paper, and to have a sour taste. In the first instance—

FIG. 45.

$$\underbrace{S}_{\text{Sulphur.}} + 2O = \underbrace{SO_2.}_{\substack{\text{Sulphur} \\ \text{dioxide.}}}$$
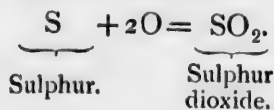
The sulphur dioxide gas when dissolved in water produces sulphurous acid, thus—

$$\underbrace{SO_2}_{\substack{\text{Sulphur} \\ \text{dioxide.}}} + H_2O = \underbrace{H_2SO_3.}_{\substack{\text{Sulphurous} \\ \text{acid.}}}$$
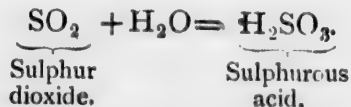
Experiment 60.—Clean the spoon used in the last experiment and place in it a very small dry piece

of phosphorus.[1]   Kindle and plunge into a jar of oxygen.   It burns with great brilliancy and produces white fumes in abundance; these deposit as a white powder on the sides of the jar, if the latter be nearly dry.   Remove the spoon and pour some cold water into the jar and shake as before.   The white substance disappears, dissolving in the water; this solution also is found to contain an acid.   The first change is thus expressed—

$$\underbrace{2P^{v}}_{\text{Phosphorus.}} + 5O'' = \underbrace{P^{v}{}_{2}O''5}_{\substack{\text{Phosphorus} \\ \text{pentoxide.}}}$$

Then—

$$\underbrace{P_2O_5}_{\substack{\text{Phosphorous} \\ \text{pentoxide.}}} + H_2O = \underbrace{2(HPO_3).}_{\substack{\text{Metaphos-} \\ \text{phoric acid}}}$$
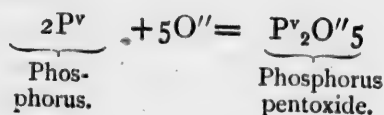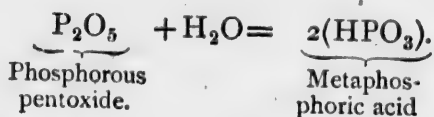
In each of these experiments, then, an oxide was the product of combustion in oxygen, and the oxide produced an acid when added to water.   The name of the element[2] signifying 'acid producer' was given in allusion to this property, but it is now known to be only one amongst several elements which can give rise to compounds exhibiting acid characters.

Experiment 61.—Take a piece of thin iron wire and coil it into a spiral, twist one end of the spiral round a small splinter of wood coated with sulphur. Now set fire to the latter and plunge the coil into a

[1] Take care to cut this under water, as phosphorus is easily ignited by friction, and it burns with great violence

[2] 'Οξὺς, acid ; γέννάω, I generate.

large jar of oxygen, as shown in fig. 46. The sulphur and the match burn and soon raise the temperature

FIG. 46.

of the iron to such a point that it undergoes strong combustion, molten drops falling from the point of wire into the water covering the bottom of the jar. When the combustion is ended, the jar is removed and the solidified drops examined. They consist of an oxide of iron, but they do not produce an *acid* with water under any conditions, nor do they exhibit any alkaline or basic characters.

$$3Fe + 4O = Fe_3O_4.$$
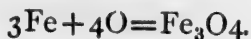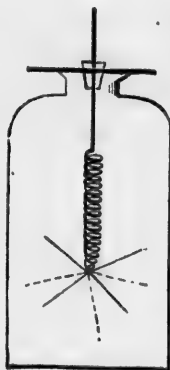
Again, when hydrogen burns in air or in oxygen, it produces *water*, which we already know to be a liquid that does not present the ordinary characters of an acid or of a base.

We thus learn that all oxides do not produce acids, though some do; further that some oxides do not produce either acids or bases, and may be classed as *indifferent* oxides.

Experiment 62.—Place a small piece of the metal sodium in the little spoon, shown in fig. 45, heat the metal until it fuses and begins to burn, plunge then into a jar of oxygen. The sodium produces a white or nearly white body (Na_2O) which dissolves in water with a hissing noise and produces a liquid which is strongly *alkaline* to test paper. Thus—

$$2Na' + O'' = Na'_2O''.$$

Sodium.　　　　　Sodium oxide.

Then—

$$Na_2O + H_2O = 2(NaOH).$$

Sodium
oxide.   Sodium hy
drate, or
caustic soda.
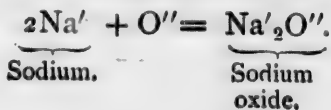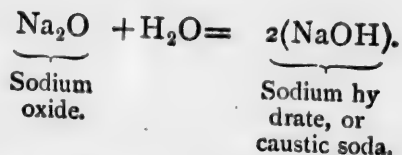
A similar experiment can be made with the metal potassium.

Experiment 63.—Finally, burn a piece of magnesium wire or ribbon in air or oxygen, and throw the white solid produced (magnesium oxide, or 'magnesia,') into a small quantity of water.[1] Although the body does not seem to dissolve in the water, the latter acquires an alkaline reaction if allowed to stand for some time, and a piece of reddened litmus paper left in the liquid becomes blue.

$$Mg'' + O'' = Mg''O''.$$

Mag-
nesium   Magnesium
oxide.

Then—

$$Mg''O'' + H_2O = Mg''(OH)'_2.$$

Magnesium
oxide.   Magnesium
hydrate.
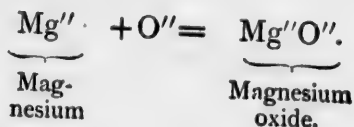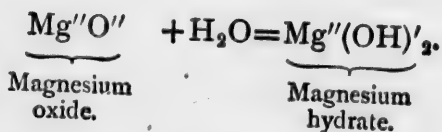
[1] Similarly a lump of common 'quicklime,' or calcium oxide—CaO—used in mortar, when added to water falls to powder and dissolves to a small extent, affording an alkaline solution or 'lime water.' If but a small quantity of water be poured over the lime, it is absorbed and the mass crumbles to a powder consisting of calcium hydrate—$Ca(OH)_2$—much heat resulting from the chemical union of the lime and water. (See further Part III.)

Our results may be thus tabulated—

Acid producing Oxides—

Carbon dioxide	.	.	.	CO_2.
Sulphur dioxide	.	.	.	SO_2.
Phosphorus pentoxide	.	.	.	P_2O_5.

Indifferent Oxides—

| Water | . | . | . | . | H_2O. |
| Iron oxide | . | . | . | . | Fe_2O_4. |

Basic Oxides —

Sodium oxide	.	.	.	.	Na_2O.
Potassium oxide	.	.	.	K_2O
Magnesium oxide	.	.	.	MgO.

The members of the first class are termed *acid anhydrides*, and those of the third class, *basic anhydrides*, because the corresponding acids and bases can yield these oxides when the elements of water are abstracted from them.

Experiment 64.—Fill a stout gas jar with water, and invert in the pneumatic trough in the usual way, introduce oxygen until one-third of the water has been displaced, and then hydrogen until the jar is filled with gas. Slip a glass plate under the mouth of the jar, remove the latter from the trough and apply a flame. A violent explosion takes place, as in the similar Experiment 23, and water is produced, as we have already proved by Experiments 24 and 25, when we exploded the mixture of gases under such conditions that the resulting water could be observed. We shall now make the gaseous mixture burn quietly.

Experiment 65.—Connect the tube *h*, fig. 47, with a small rubber cloth bag full of hydrogen by means of a flexible tube, and *o* with a similar bag containing oxygen gas, the stopcocks *s* and *s'* being closed. Apply *equal* pressure to the bags, and turn on a little hydrogen by cautiously opening the stopcock *s* ; the gas passes through the meshes of the wire gauze *g*, placed over the opening of both tubes, and enters the little chamber *c*, whence it passes by the narrow tube *t*, to the jet at which it is to be kindled. While the hydrogen burns, producing a flame 3 or 4 centimeters long, turn on the oxygen gradually by opening *s'*. The flame shortens considerably as the proportion of oxygen increases, up to a certain point, but if too much oxygen be introduced, it is extinguished with a snap, then the stopcocks must be turned off and the same plan of lighting repeated. When burning properly, the *oxyhydrogen* flame is of pale blue colour, and emits little light, but it is intensely hot—in fact the hottest known *flame*.

FIG. 47.
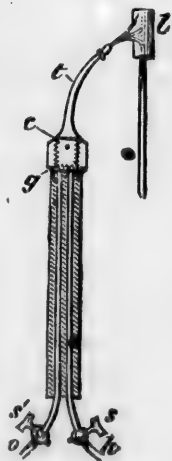
a. Introduce into the flame the end of a piece of platinum wire. The metal melts easily to a globule, though it is almost infusible in our most powerful furnaces.

b. Introduce an iron or steel wire ; it also melts quickly, and burns, emitting brilliant sparks.

c. Hold in the flame a piece of quicklime, or one of the cylinders of the same material, commonly sold

for the purpose, *l*, fig. 47. The lime does not melt, but it becomes intensely hot, almost white hot, and emits a brilliant light. This is the oxyhydrogen, or 'limelight,' which is used for various illuminating purposes.

OZONE—*Symbol*, O_3. *Molecular weight*=48.

Experiment 66.—Pour a layer of water on the bottom of a tall and wide-mouthed bottle, and introduce a stick of clean, freshly-scraped phosphorus, taking care that the latter shall not be immersed in the water through more than one-third of its length. Partially close the mouth of the vessel with a piece of card-board, and let it stand for half-an-hour or so. Whitish fumes soon appear, and ultimately fill the bottle : on opening the latter, a strong and peculiar smell is perceived, and when a strip of moist starch and potassium iodide paper [1] is plunged into the air of the bottle, it is quickly discoloured, while pure air is almost without action upon the paper. The peculiar smell and the effect upon the test paper are alike due to the presence of a small quantity of a body discovered by Schönbein in 1840, and named by him *Ozone.*[2]

The strong smell noticed when an electrical machine is worked, or electric sparks are passed through air, is due to the formation of a little ozone ; and if the oxygen evolved on the electrolysis of water, as in Experiment 22, be examined with the test-paper,

[1] Easily prepared by soaking pieces of white bibulous paper in a mixture of thin starch paste, with aqueous solution of potassium iodide.

[2] ʹΟζω, I smell.

it will also give the colour change just observed. Dr. Andrews, of Belfast, has proved that ozone is nothing but free oxygen in a remarkably active condition, for pure, dry oxygen can be partially converted into ozone by the silent electrical discharge,[1] and the oxygen during conversion is found to *contract* in volume. In fact, it has been shown that three volumes of ordinary oxygen form two volumes of ozone; the molecule of the latter therefore contains *three* atoms (unlike so many other elementary molecules, which contain two); hence, ozone may be correctly spoken of as a chemically condensed and active modification of ordinary oxygen, and its symbol written O_3. On heating ozone to 260° C. it is reconverted into ordinary oxygen, and the gas returns to its original volume, while it loses the power of affecting the test paper.

This remarkable instance of what is termed *allotropism* is not the only example of an element occurring in two forms which differ in physical and chemical characters, and yet consist of the same matter; for we shall meet, later on, with analogous allotropic forms of phosphorus, sulphur, and of carbon—the black and dull charcoal and the colourless and brilliant diamond being but allotropes of the element carbon.

Isomerism in compounds is the condition analogous to allotropism of elements; we are acquainted with pairs of compounds which contain the same elements in the same proportions, but exhibit different

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[1] Under the most favourable circumstances the proportion of ozone formed in a given volume of oxygen rarely exceeds one-tenth of the whole, even when a Siemens' or Houzeau's electrical ozoniser is employed.

physical and chemical characters ; for example, lactic acid, met with in sour milk, and solid grape sugar. But we have in two bodies, whose empirical formula is in each case CON_2H_4, illustrations of a special kind of isomerism. One of these substances, *ammonium cyanate*, is easily converted by heat into the second, a body termed *urea*, and the latter is identical with a well-known product of the animal organism. (See Appendix and Part IV. for details.)

Experiment 67.—Pour a small quantity of perfectly bright clean mercury into a short wide test tube, and lower the latter by means of a string into the jar containing ozone used in the last experiment. Note that a very short exposure to the ozonised air suffices to render the surface of the mercury dull, owing to the production of a film of an oxide of mercury. Pure oxygen does not affect pure mercury under the same conditions, but the more energetic ozone rapidly tarnishes or oxidises the metal. A piece of rubber tubing is also quickly attacked by ozone.

FIG. 48.

Experiment 68.—Bend a tube about 50 centimeters long and 1·5 c.ms. diameter into U form. Fit one opening with a cork carrying the bent gas delivery tube, as shown, fig. 48, and through the cork pass a stout platinum wire terminating within the tube in a strip of foil of the same metal. Before inserting
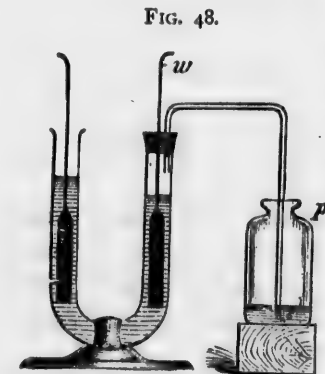
the cork, coat it (but not the platinum) thoroughly with molten *paraffin*, as the latter is not affected by ozone, and serves to protect the cork from the influence of the gas. Let the end of the small gas delivery tube dip under the surface of a small quantity of *ether* contained in the phial *p*. Now connect the wire *w* with the platinum end of a small two-cell Grove's battery, and insert the other pole in the open side of and well down into the bend of the U tube, the limbs of which have been previously half filled with water acidulated with chromic acid, or, if the latter is not available, with sulphuric acid (one volume of strong acid to three of water). Oxygen containing a little ozone will be evolved from the plate *w*, but, having no exit save from the gas delivery tube, will bubble through the ether. The latter dissolves the ozone, and after some time becomes so charged with that body that it instantly discolours the ozone test paper when a strip is dipped into the liquid. Moreover, when some of the ozonised ether is shaken up with water, coloured of a pale blue tint by 'sulphate of indigo,' the colour is destroyed, and the liquid thus bleached. Ozone is also soluble in turpentine and several essential oils, but it is dissolved to a very small extent by water : according to Carius only 0·5 c.c. in 100.

Experiment 69.—Expose a piece of ozone test paper freely to the outer air for a few hours, shading it, however, from sunshine. Even prolonged exposure to the air of a large city rarely produces discolouration of the paper, but pure country air usually causes a distinct brownish colouration in a few minutes. It

has been proved that ozone is present in pure air in minute proportions, though other bodies are occasionally met with which likewise discolour the paper. It is supposed that the blue colour of the ' sky ' is due to the presence of ozone.

It is not surprising that city air should contain but little ozone, as the organic and other impurities destroy, and, we may add, at the same time, are destroyed by the ozone, which latter, therefore, acts as a natural disinfectant by reason of its extremely energetic oxidising power.

When highly ozonised oxygen or air is inhaled into the lungs, much bronchial irritation results; but a small proportion does not produce any sensible effect.

We have thus studied in some detail the two strongly contrasted and typical elements hydrogen and oxygen—the former a type of metals, the latter of non-metals. The products of their union now require further examination at our hands, in order that we may complete the first stage of our inquiry.

CHAPTER XII.

EXPERIMENTS WITH WATER AND HYDROGEN
PEROXIDE.

OUR previous experiments having placed beyond
doubt the composition of water by weight and volume,
and its molecular weight ($H_2O = 18$), we have now to
examine some of the more prominent characters of
this most important of all liquids.

Experiment 70.—Arrange the stopperet retort A,
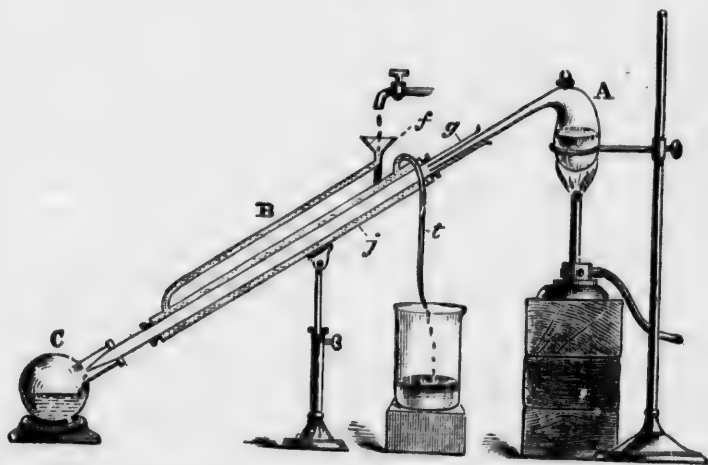
FIG. 49.

fig. 49, Liebig's condenser, B, and receiver C, as
shown. Introduce some rain or river water into A,

using a funnel for the purpose, and apply the heat of a spirit or gas flame, taking care to move the latter about at first and to wipe off drops of moisture that form on the bottom of the retort. When the water has been thus warmed at first, the lamp flame may be allowed to play steadily on the retort. After a short time the water *boils*[1] vigorously, and the steam passes into the beak of the retort, and ultimately into the inner glass tube *g*, of the condenser ; here it is cooled and condenses to water, and the latter runs into the receiver. The glass tube, passing water-tight through the tin plate jacket *j*, is cooled by a current of cold water, which enters through the funnel *f* at the lowest point of the apparatus, while the warmer and therefore lighter water, to which the steam has parted with most of its heat, is carried away by the tube *t*, at the upper part of the condenser. The first portions of the condensed steam, or *distilled water*, are to be thrown away and the rest collected in the receiver ; but it is not advisable to continue the distillation after the liquid in the retort has been reduced to one-fifth of its original volume. The water thus collected is almost chemically pure.

Water, when thus pure, is a colourless,[2] inodorous, and insipid liquid, which at ordinary temperatures

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[1] A liquid is said to boil when the temperature is reached at which the pressure (tension) of its vapour is equal to that of the atmosphere at the time. In the case of water this temperature is 100° C. at 760 mm. The temperature of ebullition depends on the particular liquid heated, and for a given liquid rises and falls with increased or diminished pressure

[2] Great masses of pure water have a distinct bluish colour.

gives off invisible vapour, and diffuses into the surrounding air ; hence, water can be slowly but wholly evaporated by simple exposure to the air. When heat is applied it can be rapidly and completely converted into steam—one volume of water affording nearly 1,700 volumes of steam at 100° C. and a pressure of 760 mm. One gram of steam at 100° C. passed into ice-cold water can raise the temperature of 537 grams of the latter 1° C. The 'latent heat of steam' is, therefore, 537 thermal units. Water becomes solid when sufficiently cooled, either by its own rapid evaporation, or by the application of external cold.

Experiment 71.—Place a few drops of pure water in a watch-glass and suspend the latter over a basin containing strong oil of vitriol, standing on the plate of an air-pump. Now cover the whole with a small bell jar and exhaust the air. As the pressure diminishes, rapid evaporation of the water takes place, while the vapour is absorbed by the oil of vitriol. The quantity of heat abstracted by rapid conversion into vapour is sufficient to cool the water down to the freezing point in a very short time, and a small piece of ice is quickly produced. Several ingenious ice-making machines have been constructed on this principle.

Experiment 72.—Take a tube about 30 c. ms. long and 4 mm. internal diameter. One end must be closed and expanded into a bulb. Pour in water until the long tube is three-fourths full. Now immerse the bulb and half the stem in a beaker of water ice cold and containing ice. The water in the stem first

rises, owing to the contraction of the glass on cooling, diminishing the capacity of the vessel and pushing up the column of water ; as the water cools, however, it contracts more rapidly than the glass, and the level of liquid sinks below the starting point until it becomes stationary and, if the external water be really ice cold, *then rises again in the tube.* If a thermometer could be plunged in the water within the bulb, it would be found to mark about 4° C. when the liquid commenced to rise. Now remove the bulb and plunge it into a 'freezing mixture'[1] of 'Glauber's salt' and common 'muriatic acid,'—the salt just covered with acid. The expansion of the liquid goes on until a sudden check is observed ; if the bulb be then removed, it will probably be found cracked and containing ice.[2] Thus water, when cooled down, contracts until the temperature of 4° C. is reached; then it *expands again up to the solidifying point*, and still greater expansion *at* that point suffices to burst the containing vessel, if it offers any obstacle to the free motion of the ice, for the latter occupies, weight for weight, more space than water at 0° C. The temperature of *maximum density* of water is 4° C., or that temperature at which one cubic centimeter of water has the greatest weight, *i.e.*, one gram.

[1] Pounded ice mixed with half its weight of common salt may be used instead, but the mixture given above is convenient and effective.

[2] This sudden expansion on freezing aids materially in the disintegration of rocks, as the water contained in the cavities and fissures, when converted into ice, expands with great force, and breaks up successive layers of the material. The same cause leads to the bursting of water-pipes.

If similar experiments are made with alcohol, oils, and other liquids, they will be found to contract but not to expand again as the temperature is reduced; thus water is the great exception to this general law, and in this respect stands alone amongst the liquids hitherto examined.

Unimportant though this property of water may seem to be, its consequences are of great moment to mankind. Thus, if water obeyed the ordinary law, our rivers and lakes would soon become masses of solid ice, their fish would be destroyed, and the heat of summer would be unable to undo the effect of the winter's cold; while the climate would probably be so altered as to render any save equatorial regions almost uninhabitable.

We thus have 'evidence of design' in this exceptional property of water, which exceeds in importance any afforded by the animal or vegetable kingdoms.

When ice at 0°C. melts, it absorbs *without elevation of temperature* as much heat as would raise the temperature of an equal weight of water from 0°C. to 79°C.[1] This quantity of heat is required to change the state from solid to liquid water. and is spoken of as its *latent heat, i.e.*, hidden (insensible) heat.

Experiment 73.—Take three Florence flasks and place in each 100 c. cs. of cold water. Weigh out roughly 50 grams of 'blue vitriol' (crystallised copper sulphate), and introduce into one of the flasks; 50 grams of red potassium bichromate, into another; and 50 grams of common salt into the

[1] Or 79 times its weight of water 1°C.

K

third. Now boil the contents of each flask : note that the copper and bichromate alike dissolve completely on boiling, each body communicating its colour to the liquid. But even long continued boiling fails to dissolve all the common salt. Therefore common salt is less soluble than the other two bodies in boiling water. As a matter of fact, bodies vary greatly in solubility : some dissolve to such a small extent that they are commonly spoken of as insoluble, for example, chalk and glass ; others so freely that they are almost indefinitely soluble, for example, caustic potash and calcium chloride.

When the contents of the three flasks are quite cold, it will be found that beautiful *crystals* have separated in the copper and the bichromate solutions, and these crystals can be made to disappear and reappear by alternate heating and slow cooling of each liquid. It is therefore evident that heat increases the solubility of both solids in water, and that the excess of solid [1] over and above that which the cold liquid can dissolve separates out, thus leaving a solution which cannot dissolve more of the particular body at the given temperature, and is therefore said to be a cold *saturated* solution. A hot saturated solution is obtained by adding the desired substance to boiling water until the solid ceases to dissolve. The

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[1] When decomposition does not accompany the act of solution, the crystals which separate from the hot solution have the same composition as the body originally dissolved. If decomposition precedes solution, as when sodium and potassium dissolve in water, Experiments 45 and 46, the body in solution must be different from that introduced.

solubility of a non-volatile solid is usually determined by evaporating a weighed quantity of its solution, saturated at a known temperature, until the solvent is completely expelled ; the dry solid residuum is then accurately weighed and the ratio of the solid to the solvent liquid thus directly determined.[1]

Experiment 74.—Pour off into a large test tube some of the cold and clear saturated solution of common salt prepared in the last experiment, now boil, and add a little dry common salt ; the latter evidently does not dissolve to any material extent, therefore the solubility of common salt in water is *nearly the same* at high and low temperatures, and in this respect salt is a remarkable exception to the general rule that solids are more soluble in hot than cold liquids.

Experiment 75.—Boil some cold and saturated ' lime water ' (see page 117) in a flask, and note that the liquid becomes turbid. This is due to the separation of some of the previously dissolved lime, its solubility in boiling water being little more than half that near to the freezing point. Lime is therefore another exception to the general rule, as it is *less* soluble at high than at low temperature.

Experiment 76.—Take four test tubes and half fill each with water. Add a few drops of alcohol to one, of chloroform to another, of oil to a third, and of glycerine to a fourth. Note that the alcohol and glycerine readily dissolve in, or mix with, the water when the contents of the tubes are shaken up, and

[1] Water saturated with one salt can dissolve others : thus a saturated solution of common salt can still dissolve either copper sulphate or red chromate of potassium.

the water can take up an indefinite quantity of each. On the other hand, agitation fails to make the chloroform or oil disappear, but when the clear water is poured off from the layer of heavy chloroform, it has the odour and sweetish taste of the latter : therefore chloroform is slightly soluble in water. The oil, on the other hand, fails to dissolve to any sensible extent.

Hence water is a good solvent for some liquids as well as for solids.

Experiment 77.—Obtain a bottle of 'soda water.' [1] On removing the pressure of the cork, a rush of *gas* takes place. When effervescence has subsided, pour some of the liquid into a flask and heat : effervescence recurs, and a cork lightly inserted in the neck of the flask is quickly blown out, owing to the escape of much gas. If the liquid be boiled and then allowed to cool, it will be found to have lost its brisk taste, due to the presence of the gas, for the latter has been wholly *expelled by heat.*

Place another portion in a beaker or tumbler, and the latter on the plate of an air-pump, cover with the bell-jar and exhaust. As the *pressure* within the receiver diminishes, strong effervescence commences in the liquid and continues as the exhaustion proceeds, until all but the most minute traces of gas are removed from the liquid.[2] It is clear, then, that the

[1] The amount of 'soda' present is usually so small that we may regard it as a solution of carbonic acid gas in water.

[2] Although the weight of any gas dissolved does not, generally speaking, diminish regularly with increase of temperature, *the weight dissolved at a constant temperature is directly as the*

gas present in this solution—called 'carbonic acid gas'—is rather freely soluble in water, unlike hydrogen and oxygen,[1] which we have already found to dissolve to an almost insensible extent; and later on (Part II.) we shall meet with much wider differences in solubility; but the fact is that all gases are more or less soluble in water.

Water, then, dissolves solids, liquids, and gases; and all our experience proves it to be the most general solvent known.

Owing to the general solvent power of water, it is not obtainable in an absolutely pure form in nature, since rain derives gaseous and even solid impurities from the air through which it passes, and from the soil on which it falls.

The prime source of all water supply is, undoubtedly, the ocean, since in nature there is a continuous circulation from the sea to the air, then from air to rivers, and, finally, to sea again. The air in contact with the ocean becomes quickly saturated with the vapour of water, and then, being carried by currents over the earth and suddenly cooled, lets fall

pressure, while the volume is the same for all pressures (Henry's Law).

The solubility of gas in water can be determined by agitating together known volumes of gas and water in a graduated tube closed by mercury, and noting the volume absorbed at constant temperature and pressure.

[1] Atmospheric air is soluble to a very small extent in water, 100 c.cs. of the latter dissolving only 1.7 c.cs. of air at mean temperature. Small though this amount seems to be, it is from this source that fish obtain the air necessary for their respiration.

much of the aqueous vapour in the form of rain.[1]
If the soil be not very porous, small streams are
formed (which wash out soluble impurities from the
surface soil), and these flowing into a common channel
produce a river.   If the soil be porous, the water
percolates through it, and may drain away again at a
lower level and form rivulets and rivers, or it sinks into
the subjacent permeable strata, thus serving to main-
tain the supply of wells and of natural springs, often
situated at a great distance from the place of rainfall.
If the permeable strata are not overlaid by those only
slightly pervious, land-springs not rising above the
surface are obtained over the district ; but if the strata
dip between two impermeable beds, an Artesian spring
is obtained on boring, at a lower level, through the
upper bed to the water-bearing strata.   Water in its
passage through the rock strata, often under con-
siderable pressure, dissolves out more or less of the
soluble constituents of the strata, and makes its
appearance in land-springs and natural or artificial
Artesian wells or springs as a mineralised water.   If
the rocks, through whose substance or fissures it
passes in its downward course to find its level, happen
to be the older metamorphic, granitic, or quartzose
rocks, or green-sand beds, but little impurity is taken
up, and the springs usually yield a supply of very
pure water. If the rocks are cretaceous, or magnesian,
or both, the water is then charged with lime and
other salts, to an extent dependent on the particular

[1] If the rainfall of a district be known, the calculations for the
catchment area can be easily made, if it be remembered that a
fall of 10 inches of rain yields 226,170 gallons per acre.

salts present in the beds, and on their solubility.[1] Water filtering through a bed of chalk dissolves but little of the latter, if the liquid be not charged with carbonic acid, since the amount of chalk (calcium carbonate) taken up bears a direct relation to the quantity of this dissolved carbonic acid. Sometimes, as in the case of the Carara springs, the water becomes charged, probably under pressure, to an unusual extent with acid and with chalk, and on issuing from the source loses much of its carbonic acid; the result of this loss is the deposition of the chalk, previously held in solution by the acid, in stalactitic forms on any objects with which the liquid comes in contact.

If, instead of passing through strata containing lime, magnesian, or alkaline salts, the water charged with carbonic acid comes in contact with decomposable ferruginous rocks, the latter yield up a portion of their iron as ferrous carbonate, which dissolves in the excess of carbonic acid, and forms the water of a chalybeate spa. These spas we often meet with in volcanic districts, and also in the neighbourhood of the coal measures. In the latter localities we rarely fail to meet not only with springs, more or less worthy of the name chalybeate, but we also find

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[1] Water rich in calcium (lime) salts is 'hard'—that is to say, it destroys much soap before a lather is produced. The 'hardness,' due to the presence of calcium (and magnesium) carbonate dissolved by carbonic acid, is removed by boiling the water, and is called 'temporary hardness;' that not removed by boiling is 'permanent hardness,' and is due to dissolved chloride or sulphate of calcium or of magnesium. See further, Part III., Calcium, and Part IV., Soap.

the sulphur spas, the sulphuretted compounds of which have been chiefly derived from the decomposition of sulphides, always present in the shales and true coal beds, by infiltrating water charged with carbonic acid.

The most celebrated of these mineralised waters of medicinal value may be thus grouped, according to their chief constituents :—

Carbonated and Alkaline, as those of Vichy, Bilin, Ems, and Malvern.

Sulphated (Sodium), Carlsbad, Cheltenham, Püllna (Magnesium), Epsom, Sedlitz.

Sulphuretted, Harrogate, Aix-la-Chapelle, Lucan, Lisdoonvarna.

Chlorinated, Leamington, Harrogate, Cheltenham, Wiesbaden, Homburg, Kissingen.

Chalybeate, Spa, Tunbridge, Harrogate, &c.

In addition to these, we meet with special products of the action of volcanic gases and steam in the—

Siliceous waters of the Icelandic Geysers.

Boracic waters of the Tuscan lagoons.

Sea water is the product of continual land washing, and in it enormous quantities of saline matter are stored.[1] An analysis of the water of the Irish Channel, made by Messrs. Thorpe and Moreton, afforded the following results :—

[1] Sea water is easily rendered potable by Dr. Normandy's process for providing pure water for ships at sea. Salt water is distilled, as in Experiment 70, but in large iron retorts (or *stills*), the salts are left in the retort, and the condensed and pure water, which is flat and insipid at first, is rendered brisk and agreeable by forcing it to dissolve some atmospheric air in a special apparatus.

1000 parts gave—

Sodium chloride	26.439
Potassium „	0.746
Magnesium chloride	3.150
„ bromide	0.070
„ sulphate	2.066
„ nitrate	0.002
Calcium sulphate	1.331
„ carbonate	0.047
Lithium chloride	traces
Ammonium „	„
Iron carbonate	„
Silica	0.005
Water	traces
	966.144

The specific gravity (or relative weights of equal volumes) of the water is 1024.8, if pure water = 1000.

The proportion of saline matter in the water of the Dead Sea is so large that the specific gravity of a recent sample proved to be 1174. (water = 1000). As the specific gravity of the human body, containing as little air as possible, is rarely higher than 1100, it follows that an average man would be buoyed up by the water of the Dead Sea, and could not sink wholly beneath its surface without some effort.

PEROXIDE OF HYDROGEN (Oxygenated Water)—*Symbol,* H_2O_2. *Mol. Weight* = 34.

Experiment 78.—Add, with frequent agitation, about 5 grams of barium peroxide (BaO_2) in powder to 30 c. cs. of diluted sulphuric acid containing 1 c. c. of strong acid; filter, and add some ether to a portion of the filtered liquid and a few

drops of solution of red potassium bichromate, and shake. Note that the ether (which is but little miscible with water) rises coloured of a magnificent blue tint, which is evanescent.

Barium peroxide and sulphuric acid afford hydrogen peroxide (or oxygenated water) and barium sulphate. The latter body being insoluble is filtered off.

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$
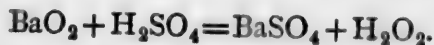
The chromic compound serves to detect the presence of the peroxide of hydrogen formed in this reaction,[1] as it is characteristic of that body to produce an unstable and highly oxidised blue chromic compound which is soluble in ether, and less quickly changes in that liquid than in any other. The solution of H_2O_2 made as above is dilute; when carefully prepared in the first instance, and then evaporated over oil of vitriol in the exhausted receiver of the air pump, a syrupy liquid of specific gravity 1452 (water = 1000) is obtained, which is colourless and inodorous, but has a strong somewhat metallic taste, and can be cooled down to —30°C. without freezing. This is the pure peroxide, but so unstable is it that a slight heat suffices for its decomposition into water and oxygen, and even the dilute solutions of the body sold are easily decomposed in the same way.

Experiment 79.—Take a long and moderately

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[1] The peroxide, like ozone, sets free iodine from potassium iodide, and therefore colours the ozone test paper. This colouration by the peroxide takes place even in presence of 'green vitriol' or ferrous sulphate, unlike that due to ozone.

thin glass tube, sealed at one end, three-fourths fill it with mercury, and the remainder with *as strong* [1] a solution of the peroxide as can be obtained : then invert in mercury, as shown, fig. 50. If the tube be inclined, and the portion occupied by the peroxide gently heated by means of a spirit or gas flame, bubbles of gas will quickly make their appearance. When sufficient gas has been collected, pass the thumb under the mercury, close the mouth of the tube, remove from the mercury, invert, and test for oxygen, by plunging a match with a glowing tip into the gas.

Fig. 50.

H_2O_2
Hg

$$H_2O_2 = H_2O + O.$$
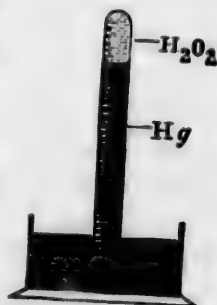
This decomposition of peroxide of hydrogen into water and oxygen gas, can be determined without the aid of heat by mere contact with—

a. Bodies which do not themselves suffer change and are therefore said to act *catalytically*,[2] for example —gold, silver, platinum, charcoal and fibrin of blood.

b. Bodies which lose oxygen at the same time as the peroxide, for example, silver oxide, and peroxide of manganese—the latter especially in presence of acid.

[1] If the solution be very dilute, little gas will be obtained. Any free acid present should be just neutralised by a few drops of caustic soda.

[2] This unmeaning term, *catalysis*, is sometimes applied to cases similar to the above, where we are at present unable to give a substantial explanation of the *modus operandi* of a body that brings about chemical changes in adjacent matter, without itself suffering sensible alteration.

Experiment 80.—Moisten a sheet of writing paper with a solution of lead acetate, and expose it to the fumes arising from a few drops of *ammonium sulphide* sprinkled over the bottom of a shallow dish. The paper becomes quickly discoloured, owing to the production of the dark-coloured lead sulphide (PbS). When stained a dark brown, remove the paper and dry it, then charge a brush with a solution of peroxide of hydrogen, and draw a design on the stained surface. The dark lead sulphide will be rapidly *bleached* by the peroxide, and the design will appear in white on a dark ground. In this case, the peroxide acts as a powerful *oxidising* agent, converting the dark lead sulp*hide* into white lead sulp*hate*, ($PbSO_4$), thus—

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$
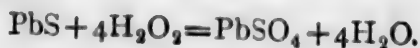
In a similar way, discoloured oil paintings and engravings can be bleached by careful treatment with dilute solutions of the peroxide. The latter has also been largely used to bleach dark hair, and change it to the golden colour, lately fashionable.

The chromic test, described under Experiment 78, is another example of oxidation effected by the peroxide, but in that case colour is developed, not destroyed.[1]

[1] Another case of oxidation by the peroxide accompanied by a colour change is the following :—Add a few drops of a fresh alcoholic solution of guiacum resin to a few c.cs. of water, then a few drops of solution of the peroxide to the turbid liquid. If to the mixture a little colouring matter of *blood* be added, a beautiful turquois blue tint is soon developed. In this case the blood determines the decomposition of the peroxide whose

Although the peroxide cannot be converted into gas, and have its specific gravity taken in that condition so as to determine its molecular weight, its analysis, and the reactions already cited, leave no doubt that its formula is H_2O_2. Its relation to water may be thus shown—

Water.
$$H-O-H \qquad \cdot \qquad \cdot$$

Peroxide.
$$H-O-|-O-H.$$

In the peroxide we assume that the two double-link oxygen atoms are united, and form a chain, to each end of which is attached a single-link hydrogen atom. If we break this chain at the dotted line, it is evident that we get two groups, each containing one atom of oxygen and of hydrogen, and each group is expressed by the symbol OH. We should not expect, and do not find, these groups to exist in the free state, because each would have one link of oxygen free, and that is contrary to the general rule ; but we might look for OH in combination. As a matter of fact we meet with the group OH in an immense variety of oxygenated compounds, and this group acts like a single atom of a monad or uni-link element, and is commonly spoken of as the ' compound radicle,' *hydroxyl.* The molecule of the peroxide of hydrogen contains two hydroxyl groups, and therefore is to be regarded as the free molecule of that body.

The study of water and peroxide of hydrogen —two distinct compounds of the same elements—leads

atom of available oxygen at once oxidises the finely divided resin into the blue coloured body. This is Dr. Day's, of Geelong, test for blood.

to the conclusion that, '*when two or more compounds of the same elements exist, combination takes place between them in proportions which are strictly multiples of the respective atomic weights.*' This is Dalton's 'Law of Multiple Proportions,' and is an obvious consequence of the atomic theory.

APPENDIX.

ALL cases of true chemical change met with in chemistry may be referred to one or other of the following divisions. As one or more examples of each kind of change occur in the foregoing experiments, the reader is advised to refer each case he has met with to its proper division. In order to facilitate this process of generalisation, a single example, with its reference, is given under each head.

1. Cases of direct combination of elements.
(EXPERIMENT 2.)

$$Mg + O = MgO$$

Magnesium.　　Oxygen.　　Magnesium oxide.
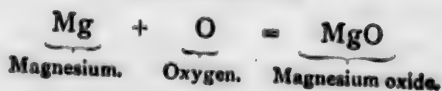
2. Cases of simple decomposition.
(EXPERIMENT 22.)

$$H_2O = 2H + O$$

Water.　　Hydrogen.　　Oxygen.

3. Cases of double decomposition.
(EXPERIMENT 14.)

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

Silver nitrate.　Sodium chloride　Silver chloride.　Sodium nitrate.
(common salt).
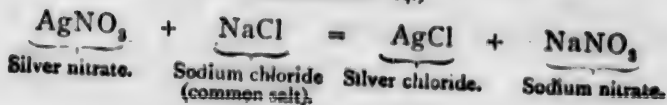
4. *Cases of decomposition by substitution.*

(EXPERIMENT 19.)

$$Zn + H_2SO_4 = ZnSO_4 + 2H$$

Zinc.   Sulphuric acid.   Zinc sulphate.   Hydrogen.
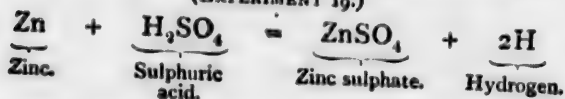
5. *Cases of decomposition by reduction.*

(EXPERIMENT 52).

$$CuO + 2H = Cu + H_2O$$

Copper oxide.   Hydrogen.   Copper.   Water.
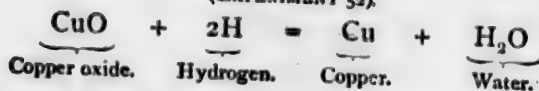
6. *Cases of rearrangement, or isomeric change.*

(PAGE 122.)

$$NH_4CNO = CO(NH_2)_2$$

Ammonium cyanate.   Urea.
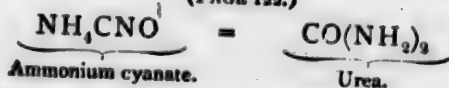
Two conditions tend so materially to determine double decomposition that Berthollet has enunciated the following ' laws ' :—

1. Two bodies in solution will always decompose each other, if it be possible, by double decomposition, to produce a new body *less soluble* than either of the two original substances.

For example—silver nitrate and common salt produce insoluble silver chloride. (Experiment 14.)

2. Two bodies when mixed or heated together will always decompose each other, if it be possible, by double decomposition, to produce a new body *more volatile* than either of the two original substances.

For example—' bread soda ' or sodium hydrogen carbonate and hydrochloric acid produce the gas carbon dioxide at ordinary temperatures. (Experiment 42.)

Exceptions to these rules exist, but these will be noticed in their proper places.

PART II.

CHAPTER XIII.

EXPERIMENTS WITH AIR AND NITROGEN.

Experiment 81.—Cut a piece of phosphorus about the size of a pea, dry it by very gentle pressure between folds of blotting-paper, and place it in the small porcelain capsule c, fig. 51, which floats on the water in the pneumatic trough. Fire the phosphorus by the touch of a hot wire, and immediately invert over it the bell-jar, which is at first full of air. The mouth of this jar must be under the surface of the water so as to completely inclose the gas it contains. Bubbles of air escape at first, owing

Fig. 51.

to expansion by the heat, but soon contraction takes place and the water rises in the jar. The white fumes produced during the combustion of the phosphorus are the same in composition as those formed in Experiment 60, *i.e.* P_2O_5, and we already know that they dissolve in water and form phosphoric acid ; thus the oxygen of the confined mass of air is removed in the form of solid oxide of phosphorus, and the latter is washed away by the water ; the gas in the jar therefore contracts in volume.   Now it is obvious that if air consisted only of oxygen, and we used sufficient phosphorus in our experiment, all the gas would disappear and water would completely fill the jar ; but, as a matter of fact, the phosphorus soon ceases to burn, and then, on allowing the jar to stand over water until the white fumes disappear, we find that a considerable volume of colourless gas remains behind.

Now transfer this gas to smaller tubes in the manner directed in Experiment 17, and make the following observations :—

a. A tube full of gas when turned up is found to be free from smell, if it has been washed thoroughly from all fumes.

b. A burning taper plunged into another tube full of the gas is immediately extinguished.

c. A little 'lime-water' shaken into another jar of gas is not rendered milky, unlike the result obtained with the carbon dioxide gas formed in Experiment 58.

Therefore air from which oxygen has been removed is colourless and inodorous ; it is incombustible, does not support the combustion of a taper,

and does not render lime-water turbid. This gas wholly consists of another elementary form of matter, which is called

NITROGEN [1]—*Symbol* N^v = 14. 1 *Vol weighs* 14 *c.grs. Molecular weight* = 28.

Nitrogen does not support animal life, and is sometimes called *azote*,[2] in consequen . It is very slightly soluble in water ; 1 c.c. of water dissolves only 0·01478 c.c. at 15° C.

Free nitrogen is one of the most indifferent gases we are acquainted with in its chemical relations, and thus contrasts strongly with the energetic oxygen. Pure atmospheric air, then, consists of these two dissimilar gases. We next have to determine the proportions in which these bodies are present in air. The rough experiment just made can give us an approximate result, for when we measure the maximum height to which the water rises in the jar after removal of the oxygen by phosphorus, we find that about *one-fifth* of the gas has disappeared. A similar, but much slower and more accurate, experiment may be made in the following way :—

Experiment 82.—Fill the graduated tube *a*, fig. 52, with 100 c.cs. of air, taking care that the volume is measured when the water stands at the same height within the tube and without in the beaker. Now fix the tube in its support, and pass high up into the confined air a small stick of phosphorus attached to a stout copper wire. Secure the wire in its place and

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[1] From νιτρον, nitre, and γενναω, I generate.
[2] α, privative, and ζωη.

leave the whole for twenty-four hours. The phosphorus slowly combines with and removes the oxygen, and leaves only nitrogen. In order to measure the

FIG. 53.

FIG. 52.

a
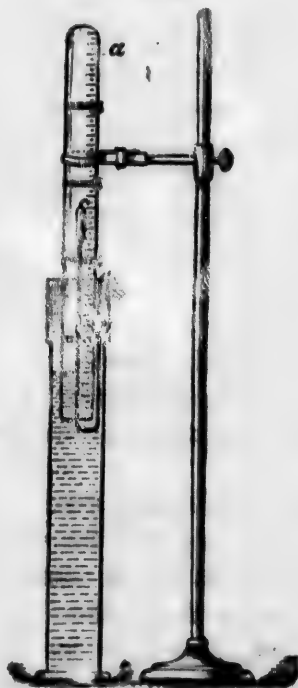
latter, withdraw the phosphorus, adjust the water-level again, and read the graduation. If the temperature and pressure are unchanged, the residual nitrogen

in the tube will measure slightly more than 79 c.cs. ; the difference, or oxygen absorbed, is, therefore, nearly 21 c.cs.

Or another, and very rapid, method of analysis by absorption may be used, which is founded upon the fact that a mixture of caustic potash and pyrogallic acid, or pyrogallol, absorbs free oxygen gas with great avidity.

Experiment 83.—Take a cylindrical tube, 1 meter long and about 16 millimeters diameter. One end is sealed, the other is closed by an india-rubber cork, through which the tube of the little bulb apparatus, fig. 53, passes. Divide the tube from the end to the cork into *six* equal parts, marking off the parts by thin elastic rings slipped over the tube. Now remove the cork and fill up to the first ring *a* with strong caustic potash solution, replace the cork, close the stopcock *s*, and fill the bulb *b* with a strong solution of pyrogallic acid ; then open the tap *s* and allow a few drops to fall into the tube (but do not let air escape). Again close *s*, press the thumb over *o*, and invert the apparatus so as to mix the caustic potash with the small quantity of pyrogallic solution, and thus to expose the gas to the action of the mixture. Bring the tube back to the position in which *b* is uppermost, remove the thumb from *o*, and cautiously open *s* ; the liquid rapidly runs in from the bulb now, as absorption has taken place. Again close *s* and proceed as before. Repeat these operations until on opening *s* only a drop or two of liquid passes into the tube, showing that all the oxygen has been absorbed. Now close *s*, fill the bulb completely with water, close *o*

with the thumb, and invert in a tall vessel of water. On opening *s* the heavier dark liquid flows out, and is soon replaced by pure water. Adjust the liquid to the same level within and without by depressing the tube to the requisite extent. The water should then stand above the *second* ring, or, on a graduated tube, at 20·9 divisions out of 100 of air.

Experiment 84.—Fill the eudiometer used in Experiment 23 with *water* in the large pneumatic trough, and allow about one-third the water to be displaced by air ; adjust the water to the same level within and without the tube, and note the volume. Now pass in half the volume of pure hydrogen gas, level again, and read the total volume. The hydrogen can be easily obtained from the apparatus used in Experiment 68 if dilute sulphuric acid be employed in it, and the wire *w* be connected with the zinc end of the battery ; gas should not be collected in the eudiometer until sufficient has been separated by electrolysis to expel all traces of air from the apparatus. The tube instead of passing into the bottle, as shown, should, of course, dip under the surface of the water in the pneumatic trough. Press the mouth of the eudiometer on an india-rubber pad placed between it and the bottom of the trough ; now grasp the tube, hold it firmly against the pad, and pass a spark between the internal wires. After explosion relax the pressure on the tube and allow water to enter ; adjust levels again and read. *One-third* of the total contraction observed represents oxygen present in the air, for we already know from Experiment 23 that two volumes of hydrogen and one volume of oxygen unite

to form water, which latter condenses at ordinary temperature.

If, in a particular experiment, 100 parts of air are mixed with 50 of pure hydrogen, and after explosion the residual gas measures 87·3 parts, the pressure and temperature being the same at the beginning and end of the operation, we can calculate the composition of air by volume thus :—The contraction after explosion is $150 - 87\cdot3 = 62\cdot7$ parts. Then $\frac{62\cdot7}{3} = 20\cdot9 -$ the

FIG. 54.
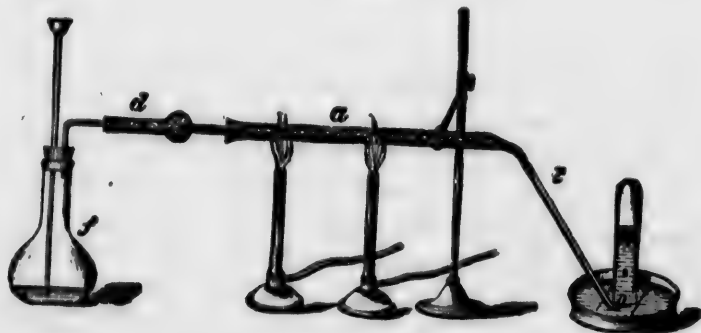
proportion of oxygen gas in the original 100 parts by volume of pure air. The difference, or $100 - 20\cdot9 = 79\cdot1$, is the percentage of nitrogen gas.

Experiment 85.—Fill the tube of hard glass, *a*, fig. 54, with bright copper turnings, support it as shown, and heat with a large gas or spirit flame ; connect the end by means of an india-rubber tube with a glass delivery tube, *t*, which latter dip under the water in the pneumatic trough. The flask *f* should only contain water enough to cover the end of the

funnel tube. Now apply heat to the tube containing the copper turnings, and when a red heat is reached pour water into the funnel tube of the flask ; air is thus made to pass over the calcium chloride in *d*, and then over the hot copper, which latter combines with the oxygen and forms dark copper oxide, CuO, while nitrogen gas bubbles from the delivery tube through the water in the trough, and should be collected in tubes and used in the manner already described.

This experiment illustrates the principle of the method adopted by Dumas and Boussingault in their precise determination of the composition of air by weight. They caused pure dry air to pass over red-hot copper contained in a glass tube, and thence into an exhausted glass globe ; each portion of the apparatus was accurately weighed before an experiment. The tube and globe were separately weighed after an experiment. The former gained in weight, owing to the combination of the copper and oxygen, and the gain of the globe was due to nitrogen ; the sum of these quantities was the weight of air operated upon. The mean of a number of laborious experiments of this kind, in which every possible precaution against error was adopted, gave the following results, which, for convenience, we compare with those of the volumetric analysis of air already described :—

Percentage of	By weight	By volume
Nitrogen	76·995	79·1
Oxygen	23·005	20·9

If nitrogen and oxygen were of the same specific

gravity, the percentage composition of air by weight and volume would be the same; but we have already seen that the specific gravity of $N = 14$ and of $O = 16$ ($H = 1$); hence as oxygen is, volume for volume, a little heavier than nitrogen, it follows that one volume of oxygen must weigh *more* than one-fifth of the total weight of five volumes of air, although oxygen forms but one-fifth by volume of the gas.

The specific gravity of pure dry air is $14^{.}47$ ($H = 1$). Therefore, one *Vol* (i.e. 112 c.cs.) weighs $14^{.}47$ c.grs.

Atmospheric air is *nearly* constant in composition. The results of numerous precise analyses of pure air, collected at various and widely-separated points of the earth's surface, and at considerable heights above sea-level during balloon and mountain ascents, prove that the variations in the proportion of oxygen are well within one-fifth per cent. by volume. In tropical countries, however, the oxygen has been observed to drop suddenly as low as $20^{.}3$ per cent., owing to some hitherto undetermined cause.

If *pure* air were a definite chemical compound of nitrogen and oxygen it should be absolutely constant in composition, and we know that it is not quite constant. therefore *it is not a definite chemical compound.* Again, oxygen and nitrogen are not present in simple atomic proportions in pure air, the ratio being $3^{.}9$ atoms of nitrogen to 1 of oxygen. If the conclusion just stated be true, a mere mixture of the two gases in the proportions indicated by analysis ought to possess all the properties of air. To test this, make—

Experiment 86.—Fill a gas jar with water and invert it in the pneumatic trough ; introduce as much nitrogen gas (prepared as in Experiment 81) as will displace four-fifths of the water, and as much oxygen (prepared as in Experiment 57) as will completely fill the jar. This is an evident mixture of the two gases, and no heat is developed, nor can we find that any other physical change accompanies the mixture —nothing occurs to indicate that any chemical action whatever has taken place between the two gases. Now remove the jar in the usual way, invert it, and plunge a match with glowing tip into the jar ; it is not rekindled as it would be in pure oxygen. Plunge a burning taper into the gas, and it continues to burn as it did in air. In fact, in all respects this mixture of the two gases acts just like atmospheric air, and all the characters of the latter are those of oxygen much diluted with just such an indifferent body as we know nitrogen to be. We thus have *synthetic* evidence in favour of the mixture view.

Experiment 87.—Take a flask capable of holding rather more than one liter, fit it with an india-rubber cork carrying the bulb tube *b*, fig. 55, but the short tube of the latter must not pass quite through the cork. *Completely* fill the flask with clean and fresh rain water, and the bulb tube also ; insert the cork carrying the latter in the neck of the flask in such a way as to have the flask and tube quite full of water. Let the delivery tube, *d*, dip under some of the same water contained in a small trough, and invert over it a test-tube filled with water. Apply heat to the flask

and gradually raise the water to the boiling point; bubbles of gas will be evolved all the time and collect in the bulb *b*; this is air previously dissolved by the water from the atmosphere. When the boiling point is reached, the steam generated pushes the air through the tube and into the test-tube placed to receive it. If the boiling be continued for some time, all the air originally dissolved in the water can be expelled and collected with little loss in the test-tube.

FIG. 55.

One liter of water fully charged with air at 15° C. should afford 17·95 c.cs., but this volume is rarely obtained.[1] If the test-tube be removed from the water, then inverted, and a burning match be now plunged into the air extracted from the water, the combustion of the wood will be much more active for a few seconds than in air We are thus led to suspect that air extracted from water contains more oxygen than ordinary air, and when analysed by any

[1] The residual water is quite flat and insipid.

of the methods already given, it is found to contain in 100 volumes :—

Nitrogen	65·
Oxygen	35·
	100·

That is to say, water dissolves more oxygen, in proportion, out of air than nitrogen, because the former is more soluble. This fact confirms the conclusion that *air is a mere mechanical mixture of the two gases,* for if it was a chemical compound the air extracted from water should have the same composition as that of the atmosphere.

Small though the proportion of air dissolved in water is, it makes all the difference between life and death to fish, as the oxygen they can withdraw from water by their respiratory organs—the gills—is essential to their existence. Hence it is necessary to secure the due aëration of water in *aquaria,* either by frequently changing or by making a number of fine streams of air-bubbles pass through the liquid.
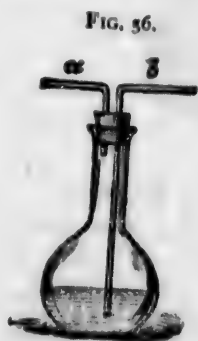
FIG. 56.

Experiment 88.—Arrange a bottle as shown in fig. 56. Put some lime-water into it, and insert the cork carrying the two tubes *a* and *b.* Apply the mouth to *a* and *inhale* or suck in air through it into the lungs; the air enters through *b* and bubbles through the lime-water, but it does not render the liquid turbid in its passage. Now apply the lips to *b*

and *exhale* air from the lungs through the tube; the air from the lungs bubbles through the lime-water, and the latter soon becomes turbid. We have already learned from Experiment 58 that the lime-water acts 'as a detector' of carbon dioxide or carbonic acid in a gas; therefore the expired air differs from that inspired by containing much carbonic acid gas.

FIG. 57.

Experiment 89.—Expired air is analysed by collecting it in a graduated tube [1] over mercury. A few drops of strong solution of caustic potash are then passed up through the mercury into the confined gas from a curved pipette, as shown in fig. 57. The carbon dioxide is quickly absorbed by the alkali in the production of potassium carbonate, thus:—

$$\underbrace{CO_2}_{\substack{\text{Carbon}\\\text{dioxide.}}} + \underbrace{2KOH}_{\substack{\text{Caustic}\\\text{potash.}}} = \underbrace{K_2CO_3}_{\substack{\text{Potassium}\\\text{carbonate.}}} + \underbrace{H_2O}_{\substack{\text{Water.}}}$$
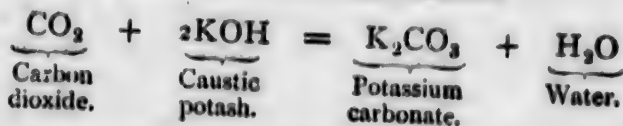
The contraction in volume observed, after adjusting for level, gives the proportion of carbon dioxide.

[1] The graduated tube is first filled with mercury and then inverted in the same liquid. A tube of glass, curved at one end like the pipette in fig. 57, is used to convey the air from the lungs into *t*. The first portions of air expelled from the mouth must be allowed to escape, and the later only collected, by forcing it through the mercury into *t*.

If a small quantity of strong solution of pyrogallic acid be now introduced, a further contraction takes place, due, as in Experiment 83, to absorption of oxygen; this is measured, and the residual gas is nitrogen, whose volume is then determined. In this way the composition of a sample of air expired by a man was found to be, in 100 volumes—

Nitrogen			79·58
Oxygen . .			16·04
Carbon dioxide			4·38
			100·00

Therefore, during animal respiration, between 4 and 5 per cent. of oxygen is consumed in the process, evidently in the combustion of carbonised material, and a nearly equal volume of carbon dioxide is evolved. An adult man thus expires about 450 liters of CO_2 in twenty-four hours.

Experiment 90.—Pour 30 or 40 c.cs. of lime-water into a wide-mouthed bottle; now plunge a burning taper or candle into the air in the bottle and let it burn for a short time; then remove the taper, close the mouth with the hand, and shake. The lime-water becomes very turbid, therefore carbon dioxide was produced during the combustion of the taper.

A similar experiment may be made with the flame of a small petroleum lamp or of coal-gas, or with a piece of red-hot coal. In all these cases carbon dioxide is a product of the combustion, and the detection of this particular product proves the presence of the element carbon in the body burned.

We have thus detected several sources of con-

tamination of air by carbon dioxide gas, and since most of these causes have been and are constantly in operation the atmosphere should have long since become hopelessly impure and even poisonous to man. We know that it is not; therefore some great natural process of purification must be constantly at work. The next experiment will help us to understand the nature of this process.

Experiment 91.—We take for our purpose one or other of the following plants— the common *Anacharis, Potamogeton natans*, to be found in our ditches and rivers, *Elodea canadensis, Ceratophyllum, Hettonia, Spirogyra*, or any whose leaves have large stomata.

FIG. 58.

Nearly fill a tall cylinder (*a*, fig. 58) with water saturated with carbon dioxide by the method described later on. Attach a portion of the plant, with as many fresh leaves as possible, to a piece of stone, in order to sink it in the water in the cylinder, and to retain it in the position shown.

Next suspend over the plant an inverted funnel, and secure it in position by means of wire stays. Fill a test-tube with water, invert and slip the mouth over the tube of the funnel, as shown. Observe now that no change takes place in a feeble light, but expose the whole arrangement to bright sunshine for some hours and bubbles of gas will be evolved, and
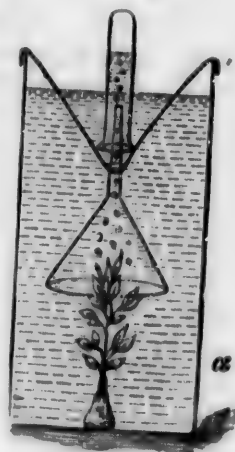
will rise through the funnel and collect in the test
tube.   When a sufficient quantity has been collected,
remove the tube in the usual way, invert it, and
plunge into the·gas a match with a glowing tip ; note
that it is rekindled.   The gas can be easily identified
as pure oxygen thus evolved from the plant.   A care-
ful examination of this process of separation of oxygen
has shown that the latter is a product of the decom-
position of CO_2 in the green or *chlorophyll* cells cf
the leaves ; in these cells the carbon is fixed and em-
ployed in the production of various carbonised bodies,
starch, woody fibre, &c., while any oxygen not re-
quired for similar purposes in the plant-organism is
returned to the atmosphere in the gaseous form,
as we have seen.[1]   We learn, thus, that the carbon
dioxide which issues from the lungs of a man or other
animal, from the burning candle, the factory fire, and
many other sources, and that would, if allowed to
accumulate, soon render the atmosphere deadly to the
higher animals, is rapidly decomposed by vegetation
under the influence of the solar rays.   Thus man is
saved from slow poisoning by the depurating action of
vegetation on impure air, and this action is, moreover,
the chief cause of the nearly constant composition of

[1] In addition to this decomposition of carbon dioxide, which
is only effected in the chlorophyll cells under the influence of
light—and chiefly of the yellow rays—a process of *respiration*
analogous to that of animals takes place in all parts of the
plant, and is not dependent on the action of light ; but this ab-
sorption of oxygen and evolution of carbon dioxide is so very
feeble that the loss of carbon involved is insignificant when
compared with the enormous gain of carbon by decomposition of
its dioxide in the chlorophyll cells.

the air, aided as it is by the action of atmospheric currents arising from alterations of temperature, and the operation of a curious physical law in virtue of which the constituents of a gaseous mixture tend to diffuse or distribute themselves equally throughout the mass. This principle can be easily illustrated by the following experiment.

Experiment 92.—Fit the double-necked bottle *h* as shown in fig. 59. The tube *t* passes through the cork nearly to the bottom of the bottle, where it dips just under the surface of some water coloured with litmus or co- chineal ; this tube is drawn out to a rather fine jet at the end *e.* Both corks are best of india-rubber ; through the second passes the long tube *m* ; this, like *t*, should just dip under the surface of the water in *h.* The end outside the bottle passes airtight through the cork *c*, which closes the porous earthenware cell *s.* The latter is one of the small porous cells used for galvanic batteries, and should be new and clean. All the corks, if not of rubber and very tight, must be coated with paraffin. Having prepared the apparatus, fill a rather large jar with hydrogen, and bring it mouth downwards over *s.* Almost immediately gas bubbles from *m* through the liquid in the bottle, and as it has no exit it is confined in *h* and exerts considerable pressure upon the surface of the coloured water, which latter is, in consequence, driven up through *t* and issues from *e*, forming a temporary fountain. On

FIG. 59.

M

withdrawing the jar the reverse action takes place—air enters through *t*, and the liquid rises in *m*.

The reason for the accumulation of gas within the apparatus at first, and consequent increase of pressure, is that the hydrogen rapidly diffuses itself through the air in the cell and *vice versâ*, while the porous cell walls do not oppose material obstacles to this process of diffusion, though sufficient to intercept mere currents. But hydrogen gas, being so much lighter than air (in the ratio of 1 to 14·47), rushes through the pores at a higher rate than the heavier air can pass in the oppo-site direction—consequently gas accumulates in the cell, and the evidence of this is the increased pressure within the apparatus, which suffices to raise a column of liquid to a considerable height. If oxygen were present at first in the cell, the pressure would be still higher, owing to the greater specific gravity of that gas. The law regulating this diffusion of gases is called 'Graham's law,' as it was discovered by the late Professor Graham, the last scientific Master of the British Mint, and its statement is that *the diffusion rates of two masses of gas in contact are inversely pro-portional to the square roots of their specific gravities.* Thus, comparing hydrogen and oxygen, the specific gravity of the latter is 16, and the square root of 16 is 4—therefore, according to the law, four times as much hydrogen as oxygen will pass through the cell wall in a given time.

In the case of air the two constituents do not diffuse out into the external hydrogen at the same rate, the heavier oxygen passing out in the above proportion, and the somewhat lighter nitrogen at a higher rate.

IMPURITIES IN AIR.

The impurities commonly met with in air are the floating solid particles—the 'motes in the sunbeam' beautifully seen when a beam of sunlight passes through the air—and the gaseous or vaporous bodies we should expect to find, viz., carbon dioxide, water, ammonia, and ozone ; while we occasionally meet with carbon monoxide, marsh gas, and other hydrocarbides, sulphur dioxide, sulphuretted hydrogen, oxides of nitrogen, chlorine, and organic emanations from the skins and lungs of men and other animals.

Experiment 93.—Expose in a dish a quantity of lime water to the air of some open space for a few hours ; the water will soon be covered with a white pellicle, owing to the formation of chalk arising from the action of the carbon dioxide, always present in ordinary air, upon the lime in the water (see Experiment 58).

The usual proportion of CO_2 in good fresh air is from 0·033 to 0·04 per cent., i.e. 3 to 4 parts in 10,000, but the air of confined and ill-ventilated spaces is often much less pure, as it is rapidly altered by animal respiration and burning illuminating materials.

An adult man expires about sixteen cubic feet of air per hour, and about $\frac{1}{50}$th of this is carbon dioxide. A single gas-jet which consumes three cubic feet of coal gas per hour (equal to about 150 grams of oil or fat) uses up more air than two men.

When the proportion of carbon dioxide reaches 0·09 to 0·1 per cent., the air is close and ' fusty ' to the senses, and is unwholesome. The late Dr. Parkes

held, and we think rightly, that air should be con-
sidered unwholesome for human beings when the
carbon dioxide present exceeds 0·06 per cent., or 6
volumes in 10,000, the carbon dioxide being in this
case taken as a measure of the general purity of the
atmosphere.[1] Good ventilation aims at keeping the
atmosphere of a room well under this standard, and
for this purpose 3,000 cubic feet of fresh air must be
introduced per head every hour, and about twice
this volume of fresh air per hour for each gas-burner
that hourly consumes three cubic feet of coal gas, un-
less the products of combustion are removed by
special means.[2]

Experiment 94.—Take two plates ; expose to the
air on one some lumps of calcium chloride, and on
the other some common pearlash—impure potassium
carbonate. After a time both substances will be found
in a moist condition, having absorbed aqueous vapour
from the atmosphere and dissolved in it, or *deli-
quesced* ; if exposed long enough each will become
completely liquid, and a strong solution of calcium
chloride be formed in one case and of potassium car-
bonate in the other. Both substances are spoken of
as *hygroscopic*, or moisture-imbibing bodies, and thus
serve to prove the presence of water in the air.

[1] Two methods will be found in Chapter XX. for the esti-
mation of CO_2 in air.

[2] The amount of air-space required for healthy adults in a
room is at least 300 cubic feet per head ; but it is well to aim at
a higher proportion. A room 12 feet long, 10 feet wide, and
10 feet high contains, when free from furniture and inhabitants,
1,200 cubic feet of air, and will therefore accommodate four
healthy adults if adequate ventilation be provided.

Experiment 95.—Place a few pieces of ice in a test-tube ; the sides of the latter are soon cooled down nearly to the temperature of melting ice, and in turn they cool the air immediately in contact with the exterior of the tube ; moisture is then seen to be deposited on the glass, because air nearly saturated with aqueous vapour at a comparatively high temperature deposits much of its water when cooled nearly to the freezing point, or to any temperature below that at which the amount of vapour actually present would suffice to saturate it.[1] In nature, when this saturation point is passed, the excess separates in the form of dew, cloud, or rain. Therefore, by the attraction of deliquescent bodies and by the method of cooling, we learn that ordinary air contains aqueous vapour ; the amount of this is, however, extremely variable.

Experiment 96.—Fill a large glass beaker capable of holding two or three liters with fresh and clean rain water ; add to the water about 10 c.cs. of *Nessler test* solution,[2] and let the mixture stand after mixing. Few samples of rain water fail to show a pale yellow colour when treated with the test, which latter is the most delicate reagent for ammonia that we are acquainted with.[3]

[1] Air but three-fourths saturated with moisture is in the best condition for respiration. See Chapter XX. for estimation of moisture in air or other gas. A work on physics must be consulted for the general subject of *Hygrometry*.

[2] The preparation of this solution is described under Iodine, See page 244.

[3] So delicate is this test that it will indicate the presence of 1 part of ammonia in 10,000,000 of water.

The ammonia (NH_3) in air rarely exceeds one part in one million; but this minute proportion, when carried to the soil by means of rain, amounts to between 5 and 6 lbs. per acre annually, and from this source vegetation on uncultivated soils derives some of the nitrogen necessary for healthy development, though, as the elaborate experiments of Messrs. Lawes and Gilbert at Rothamstead have shown, the agricultural importance of this aerial ammonia has probably been exaggerated.

We have already (Experiment 69) learned how to test for ozone in air, and the characters of the other accidental constituents of the atmosphere already enumerated will best be dealt with under the several compounds.

CHAPTER XIV.

EXPERIMENTS WITH COMPOUNDS OF NITROGEN.

THE element nitrogen has been so named (see p. 147) because it produces *nitre*, and is a characteristic constituent of that body. This nitre is a white crystalline compound which is found on analysis to contain

FIG. 60.
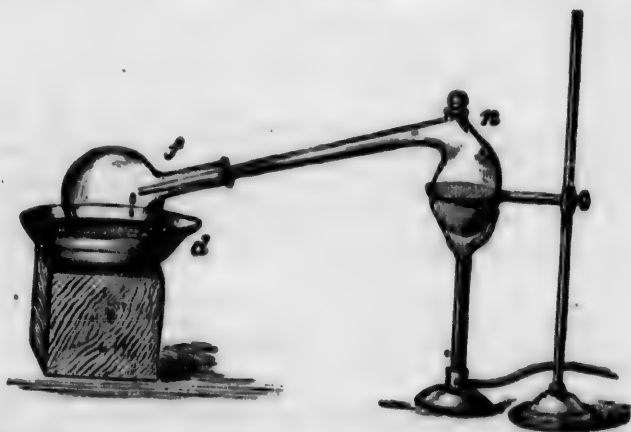
nitrogen, potassium, and oxygen, in the proportions indicated by the formula KNO_3.

NITRIC ACID $= HNO_3$.—*Molecular weight* $= 63$.

Experiment 97.—Place in a tubulated retort n, fig. 60, about 30 grams of nitre and well cover it with

MICROCOPY RESOLUTION TEST CHART
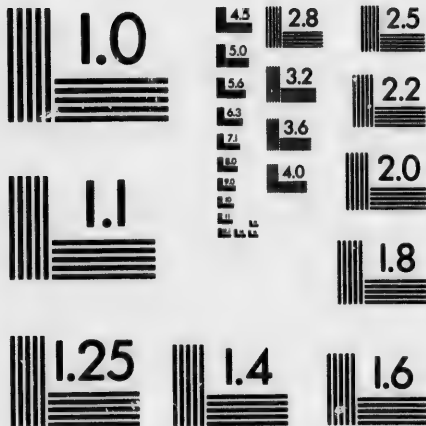
(ANSI and ISO TEST CHART No. 2)

APPLIED IMAGE Inc

1653 East Main Street
Rochester, New York   14609   USA
(716) 482 – 0300 – Phone
(716) 288 – 5989 – Fax

strong sulphuric acid; connect the retort directly with the receiver *f*, which latter is supported by the dish *d* containing cold water ; gently heat the retort and raise to the boiling point; a heavy fuming liquid of a yellow colour distils over and collects in the receiver, which latter should be occasionally cooled by pouring water over it.   When the distillation is at an end allow the apparatus to cool, when the residue in the retort will solidify to a crystalline mass easily dissolved out by water, and consisting of acid potassium sulphate, $KHSO_4$.   The contents of the receiver are now to be examined.

a. Allow a drop of the liquid to fall on a piece of blue litmus paper ; the latter is instantly coloured red and then bleached, while the paper is soon destroyed—therefore the liquid is a strong and corrosive *acid.*

b. If a piece of white silk, some wool, or cork be immersed in the acid it is quickly coloured yellow, and, in the case of the cork, soon destroyed.   The skin is likewise corroded and stained yellow by the acid.

c. Add a few drops to a solution of *indigo* ; the blue colour of the latter is instantly changed to a dirty brown.

d. Place a few fragments of copper in a test-tube and pour over the metal a small quantity of the acid. Deep ruddy fumes are rapidly evolved, and a blue liquid remains in the tube.

The acid possessing these characters is nitric acid, or *aqua fortis*, whose formula when pure is HNO_3.

The following equation represents the change that

takes place when nitre and sulphuric acid are heated together—

$$\underbrace{KNO_3}_{\substack{\text{Potassium}\\\text{nitrate.}}} + \underbrace{H_2SO_4}_{\substack{\text{Sulphuric}\\\text{acid.}}} = \underbrace{HNO_3}_{\substack{\text{Nitric}\\\text{acid.}}} + \underbrace{KHSO_4}_{\substack{\text{Potassium and}\\\text{hydrogen sulphate.}}}$$
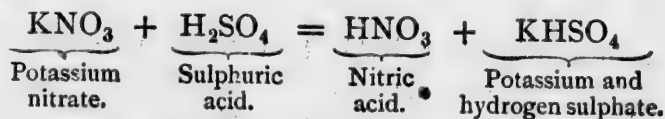
On the large scale the cheaper sodium nitrate ($NaNO_3$) or 'Chili nitre' is used instead of the potassium compound ; moreover, in order to avoid waste of sulphuric acid, two molecules of the nitre for one of acid are used, but the heat required to complete the operation is much higher than that employed in the Experiment 97, and the residue in the large retorts used is neutral sodium sulphate, Na_2SO_4—

$$2(NaNO_3) + H_2SO_4 = 2(HNO_3) + Na_2SO_4.$$

Pure nitric acid has a specific gravity of 1·510 (water = 1·000).[1]

The best commercial acid is a colourless liquid of specific gravity 1·420, and contains about 30 per cent. of water. When exposed to the air it emits an acrid corrosive vapour, and begins to boil when heated to 121° C.

The acid is distinguished by the characters and tests already observed, and we have in the copper test (*d*) an experiment illustrating the fact that nitric acid is a powerful oxidising agent, since it easily suffers deoxidation to a low oxide of nitrogen, to-

[1] The colour of the ordinary acid is due to the presence in solution of oxides of nitrogen ; these can be removed by making a stream of air bubble through the acid. Other impurities often found in the commercial acid are sulphuric and hydrochloric acids ; for their tests see the respective acids.

gether with loss of hydrogen. In the case of copper the reaction in the *strong* acid may be thus written—

$$2Cu + 6HNO_3 = N_2O_3 + 2(Cu(NO_3)_2) + 3H_2O.$$

Copper.   Nitric   Nitrogen   Copper   Water.
          acid.   sesquioxide.   nitrate.
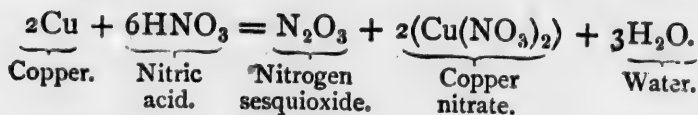
The ruddy fumes observed in the experiments consist in part of the sesquioxide of nitrogen, and the blue liquid formed contains in solution the blue-coloured copper nitrate,[1] which latter can be separated by evaporation and crystallisation.

Experiment 98.—Put a lump of red-hot charcoal on any suitable support under a flue. Take up a few drops of strong nitric acid in a long glass tube and allow the acid to fall on the charcoal. Note that violent action at once takes place, the charcoal burning rapidly in the oxygen of the acid.

Experiment 99.—Add some of the acid to a solu tion of ferrous sulphate or 'green vitriol;' it at once communicates a *black* colour, which is changed to brown on boiling.[2] This is the *iron* test for nitric acid.

Experiment 100.—Place a crystal of the alkaloid *Brucia* on a white plate and let fall a drop of the strong acid upon it. Note that a fine *orange red* colour is developed.

Experiment 101.—Place a few cubic centimeters of nitric acid in a capsule, and add caustic potash solution until the acid is neutralised ; then evaporate

[1] For the action of the weaker acid on copper, see page 179.
[2] For the explanation of this, see page 180.

until a pellicle forms and allow to stand. On cooling crystals of nitre separate—

$$HNO_3 + KOH = KNO_3 + H_2O.$$
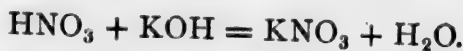
The analyses of nitric acid and of nitre lead to the formulæ just given as the simplest expressions for their composition ; but the discussion of the analytical data cannot tell us whether nitric acid may not be represented by the symbols — $H_2N_2O_6$, and nitre by $K_2N_2O_6$, or some multiples of these values. Moreover, the vapour of nitric acid is so easily decomposed by a high temperature that Avogadro's law cannot help us to decide between the above formulæ. How then are we to proceed in order to determine which of the formulæ, HNO_3 or $H_2N_2O_6$, for example, is correct— in other words, whether nitric acid is *mono-* or *di-basic*? (See Part I. page 84.) A little consideration will satisfy us that if the acid be di-basic and its formula $H_2N_2O_6$, it ought to be possible to form a second potassium salt—one containing KHN_2O_6. We must, therefore, make an experiment calculated to determine this point.

Experiment 102.—Take two porcelain capsules perfectly clean and dry, and place one on each pan of the balance and counterpoise exactly; then mark one capsule A and the other B, so as to know which pan it belongs to. Remove the capsules and place in each 10 c.cs. of the same strong solution of caustic potash coloured blue by the same quantity of solution of litmus. Now neutralise the potash in A by nitric acid added gradually, without loss, from any convenient measuring vessel. Note the quantity required for this

purpose. Next add to the caustic potash in B *double* the quantity of the nitric acid required to just neutralise the first. Place the two capsules close together on a small tray of sheet iron, the bottom of which is covered with a layer of sand, and heat this 'sand bath' by means of a gas or spirit flame underneath, so as to make the liquid in each capsule slowly evaporate without boiling or spirting. When the solutions have been concentrated to the same extent small crystals separate ; no difference is observed in the appearance of these or in their apparent amount, but during evaporation acid fumes are freely evolved from B. Continue the gentle heat until a dry mass is left in each capsule and acid vapours are no longer given off ; then, when cold, replace the capsules in their respective balance-pans. If the operations have been carefully conducted the capsules should still counterpoise, proving that the *same weight* of matter was produced in each case ; and when each residue is carefully examined it is found to possess all the characters of nitre. If it were possible to form the salt KHN_2O_6, it should have been produced in B and detected there by a great gain in weight and by differences in the characters of the salts obtained in the two capsules. No new salt is separated, but merely a mixture of nitre and excess of nitric acid is obtained, and the latter being volatile is driven off during evaporation. Therefore nitric acid is a monobasic acid, and its formula must be written HNO_3.

Experiment 103.—Introduce into a test-tube some copper turnings and nitre, add enough water to dissolve the latter, and heat. No fumes will be evolved.

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to dis-
olved.

Cool the liquid and add a cubic centimeter or so of oil of vitriol ; violent action soon begins and ruddy fumes are freely evolved, just as in Experiment 97, *d.* In this case the metallic nitrate is inactive ; but on addition of the powerful sulphuric acid the salt is decomposed as in Experiment 97, and the nitric acid thus set free at once produces its characteristic effects. For a similar reason a metallic nitrate reacts, as in Experiments 99 and 100, only after the addition of sulphuric acid ; hence this addition cannot be neglected in testing a salt of nitric acid.

Experiment 104.—Mix a very small quantity of nitre with about one-third of its weight of powdered charcoal in a small porcelain crucible, and apply heat. Violent action almost amounting to explosion takes place ; the mixture is said to ' deflagrate '—the carbon or charcoal burning in the available oxygen of the nitre. All nitrates[1] cause this deflagration. When sulphur as well as charcoal is mixed with nitre, *gun-powder* is produced. The proportions of the ingredients differ somewhat, according to the purpose for which the powder is to be employed, but the percentage composition of good rifle powder is—

Nitre					75
Sulphur					10
Charcoal					15

Such a powder when fired affords about 280 times its volume of gas, corrected to 0° C. and 760 m.m. ; and this gas is found to be a somewhat variable mixture of nitrogen, carbon dioxide, and

[1] For the characters of particular nitrates, see Part III.

carbon monoxide gases, with much smaller pro-
portions of other gaseous bodies. A solid residue,
rich in potassium sulphide, results from the decom-
position, and this, when blown out into the air from
the muzzle of a gun, quickly burns and forms potas-
sium sulphate, of which the white smoke chiefly
consists.

By the action of phosphoric anhydride on strong
nitric acid, colourless crystals can be obtained con-
taining N_2O_5. This is nitrogen pentoxide, or nitric
anhydride, and when added to water it reproduces
nitric acid thus—

$$N_2O_5 + H_2O = 2HNO_3.$$

The same anhydride is produced when dry chlo-
rine gas is conducted over dry silver nitrate; silver
chloride and oxygen are likewise obtained—

$$2AgNO_3 + 2Cl = 2AgCl + N_2O_5 + O.$$
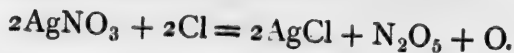
Poisonous action—Strong nitric acid is a powerful
corrosive, colouring the skin or mucous membrane
yellow, and destroying the tissues. When swallowed
it acts as a strong irritant poison and produces violent
vomiting, great pain, loss of voice, difficulty of breath-
ing, and ultimate death. When much diluted with
water the acid can be safely taken in small quantity.
Antidotes.—Calcined magnesia or dilute solution of
borax, followed by oily or mucilaginous drinks.

Nitrogen Peroxide=NO_2 or N_2O_4. *Mol. weight*=46.

Experiment 105.—Take a tube of hard glass
closed at one end (*b*, fig. 61). Having introduced

about 10 grams of dry and powdered lead nitrate into *a*, bend the tube in the form shown ; then apply heat to the salt ; presently deep orange fumes are given off, and these pass down the tube *b*; if the bend *c* be immersed in a freezing mixture of ice and salt, or a mixture of hydrochloric acid and sodium sulphate,

FIG. 61.
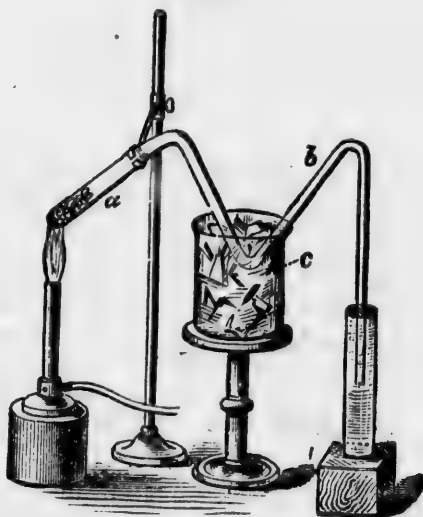
the fumes condense and form drops of a blue liquid, which solidifies to a white crystalline mass if cooled to − 10° C. This body is an oxide of nitrogen whose formula in the state of gas is NO_2,[1] though often written N_2O_4 for reasons that will be stated when considering another oxide of nitrogen.

[1] When electric sparks are passed for some time through dry air, a mixture of oxides of nitrogen is formed, amongst which this body occurs.

The decomposition of the lead nitrate is thus re-presented—

$$\underbrace{Pb''(NO_3)_2}_{\text{Lead nitrate.}} = \underbrace{2NO_2}_{\substack{\text{Nitrogen}\\\text{peroxide.}}} + \underbrace{PbO}_{\substack{\text{Lead}\\\text{oxide.}}} + \underbrace{O}_{\text{Oxygen.}}$$
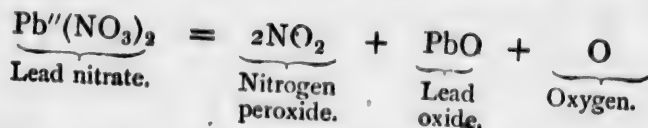
The oxygen gas is mixed with the nitrogen peroxide.

a. As the gas issues from the delivery tube make it bubble through *oil of vitriol.* Note that much of the ruddy fumes dissolve in the acid, the oxygen escaping.

b. Pass some bubbles through solution of *potassium sulphocyanate*, a transient red colour is produced.

c. Pass the gas into a small quantity of ice-cold water; it is absorbed and an *acid* liquid is obtained. NO_2 is not an acid anhydride, but it affords a mixture of acids which are directly related to two other oxides of nitrogen, thus—

$$2NO_2 + H_2O = \underbrace{HNO_3}_{\substack{\text{Nitric}\\\text{acid.}}} + \underbrace{HNO_2}_{\substack{\text{Nitrous}\\\text{acid.}}}$$
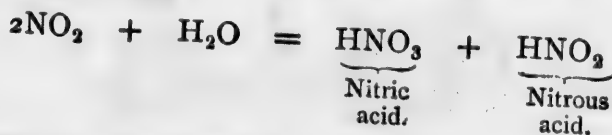
NITROGEN SESQUIOXIDE OR NITROUS ANHYDRIDE $= N_2O_3$. *Molecular weight*$=76$.

NITROUS ACID$=HNO_2$. *Molecular weight*$=47$.

Experiment 106.—Introduce a gram or two of white arsenic (As_2O_3) into a tube similar to *a b*, fig. 61; add some nitric acid diluted with half its volume of water. On the application of a gentle heat brown fumes are given off; these, if cooled below 0° C., afford a blue liquid, or when passed into ice-cold water, a blue

solution is obtained. The formula of the body is N_2O_3. The reaction which affords it is thus expressed—

$$2HNO_3 \; + \; As_2O_3 \; + \; 2H_2O$$
$$= \underbrace{N_2O_3}_{\substack{\text{Nitrogen} \\ \text{sesquioxide.}}} \; + \; \underbrace{2(H_3AsO_4)}_{\substack{\text{Arsenic} \\ \text{acid.}}}$$
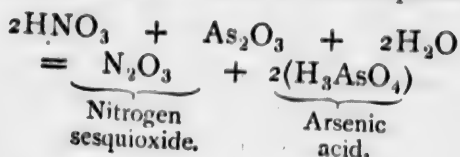
The arsenic acid remains in the tube. We have already seen (Experiment 97) that nitrogen sesquioxide forms a considerable portion of the gas evolved when *strong* nitric acid acts on copper.

a. Pass the oxide into water, and note that an *acid* solution is obtained, and this is found to contain but a single acid. In this respect N_2O_3 acts as an anhydride, like N_2O_5, and affords a definite but very unstable monobasic acid, *nitrous acid*,[1] with the elements of water—

$$N_2O_3 \; + \; H_2O \; = \; \underbrace{2HNO_2}_{\substack{\text{Nitrous} \\ \text{acid.}}}$$
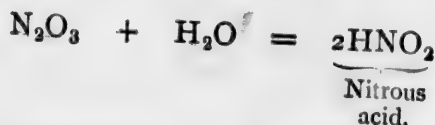
It will be remembered that this is one of the two acids already known to result from the action of NO_2 on water.

b. Add a few drops of the solution of nitrous acid to water coloured by a little Condy's fluid (solution of potassium permanganate, a body rich in oxygen with which it easily parts, and then loses its fine purple

---

[1] The terminal *ous* as applied to an acid is always employed to indicate a less oxidised body than one whose name ends in *ic*. In the above case, nitrous contains less oxygen than nitric acid.

colour) ; the solution is decolorised and the *nitrous* converted into *nitric* acid, thus—

$$HNO_2 + O = HNO_3.$$
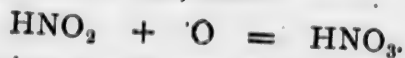
Therefore nitrous acid can act as a deoxidising or *reducing* agent. Now prove that nitric acid in dilute liquids does not decolorise the permanganate, by making a corresponding experiment.

c. Add a few drops of the nitrous acid to 200 or 300 c.cs. of water containing a little potassium iodide in solution and some starch paste—a *blue* colour will be produced if the solution be very dilute, or a greenish brown if strong. The colour is due to the element iodine which is set free by a portion of the nitrous acid, and then produces a strongly coloured 'iodide of starch.' In this case nitrous acid acts as an *oxidising* agent, thus—

$$HNO_2 + \underbrace{KI}_{\substack{\text{Potassium} \\ \text{iodide.}}} = \underbrace{I}_{\text{Iodine.}} + \underbrace{KOH}_{\substack{\text{Potassium} \\ \text{hydrate.}}} + \underbrace{NO}_{\substack{\text{Nitric} \\ \text{oxide.}}}$$
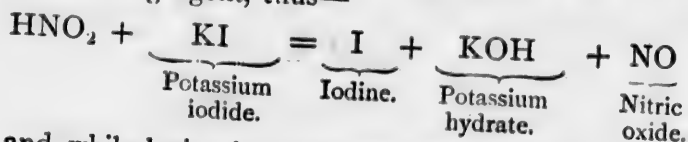
and, while losing its hydrogen, parts also with an atom of oxygen, and is reduced to the lower oxide of nitrogen—nitric oxide. Another portion of the nitrous acid neutralises the potassium hydrate liberated in the above reaction.[1]

NITRIC OXIDE $= NO$ or N_2O_2. *Mol. weight* $= 30$ or 60.

Experiment 107.—Take the bottle, fig. 62, used

---

[1] Pure dilute nitric acid does not afford this reaction, and the two acids may therefore be distinguished by its means. In the application of this test to the detection of *nitrites* in well water the latter must be acidified with acetic acid.

in the preparation of hydrogen gas, and introduce some copper turnings or wire into it, cover the metal with some warm water, and insert the cork carrying the thistle funnel. Now pour down the funnel tube a little strong nitric acid. Chemical action soon commences and much gas is evolved ; the first portions are allowed to escape, and the gas is then collected as usual in the jars. As the evolution of gas slackens, a

FIG. 62.
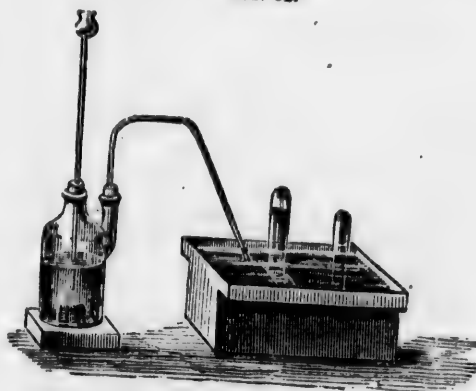
little more acid will make it brisk again. The jars of gas should be allowed to stand over the water for a short time in order that the brown fumes of N_2O_3 that generally accompany it may dissolve in the water and leave the gas colourless.

This gas is nitric oxide—NO, produced in the following reaction with the somewhat *diluted* acid—

$$3Cu'' + 8HNO_3 = \underbrace{3Cu''(NO_3)_2}_{\text{Copper nitrate.}} + \underbrace{2NO}_{\text{Nitric oxide.}} + 4H_2O$$

N 2
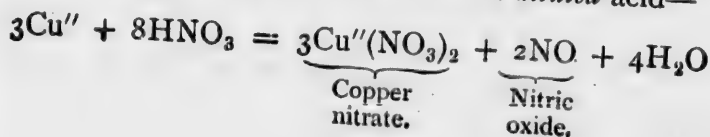
a. Remove a jar full of the colourless gas, covered with its glass plate as usual. Withdraw the plate, and note that brownish fumes are instantly produced when the gas meets the air. This is the most characteristic property of the gas, as it rapidly passes into one or other of the higher oxides of nitrogen—N_2O_3 or NO_2—on meeting with a sufficient proportion of *free* oxygen.

This property is of the utmost importance in the manufacture of oil of vitriol.

b. Place a piece of phosphorus in the spoon, fig. 63, and touch it with a warm wire; while it is

Fɪɢ 63.

just kindling or burning feebly, plunge it into a jar of nitric oxide—the flame is almost or quite extinguished. Now withdraw and again kindle, but let the phosphorus burn briskly, then plunge into another jar of the gas; vivid combustion now takes place. In the first case, the temperature was not sufficiently raised to decompose the gas and render its oxygen available; in the second this decomposition occurred, phosphoric anhydride was produced, and free nitrogen left. Similar experiments may be made with sulphur and wood.

c. Make a strong solution of ferrous sulphate (green vitriol) in water and pour the solution into a jar of the gas, close the mouth quickly with a glass plate or the hand, and shake. Note that absorption occurs, as the plate or hand is drawn tightly up to the mouth of the jar, and the contents of the latter become *dark-coloured*. Therefore the gas is easily soluble in solution of ferrous sulphate, though 100 c.cs.

of pure water dissolve only 5 c.cs. of the gas. A definite compound is formed in solution whose formula is $NO, 2FeSO_4$. If the dark liquid be boiled the nitric oxide is driven off as gas, and a somewhat brownish solution left. The above dark-coloured compound is formed in testing for nitric acid by ferrous sulphate (Experiment 99), the latter first deoxidises the nitric acid and the chief product of reduction—nitric oxide—then dissolves in the excess of sulphate.

Experiment 108.—Fill a tube of the form shown, fig. 64, with mercury, and invert in mercury in a stout tumbler; now introduce as much nitric oxide gas as will about half fill the tube. Pass up into the gas, through the mercury, a pellet as large as a pea of the metal potassium (the latter

FIG. 64.

should be dried from adherent naphtha by blotting paper, and the surface then scraped clean with a knife). By closing the mouth of the tube under the mercury with the thumb, and giving a jerk, the potassium can be thrown into the end *a* without leaving any mercury there. Remove the thumb, keeping the tube still under the surface of the mercury and the end *a* depressed as shown, then apply heat to the potassium; the metal melts and quickly combines with the oxygen of the nitric oxide, leaving pure nitrogen gas. Allow the apparatus to cool and note that the mercury has risen in the tube. If the experiment be properly conducted the volume of gas is
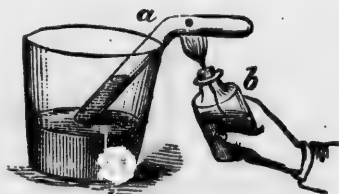
reduced *one-half* ; therefore nitric oxide contains only half its volume of nitrogen—that is to say, the molecule of nitric oxide contains but a semi-molecule (one atom) of nitrogen. We are not, however, justified in assuming that it contains only half its volume, or one atom, of oxygen ; hence another experiment is necessary.

Experiment 109.—Place some copper turnings in a glass tube similar to that used in Experiment 52. Heat the copper strongly, and pass over the metal a slow current of nitric oxide. Note that the copper is

FIG. 65.
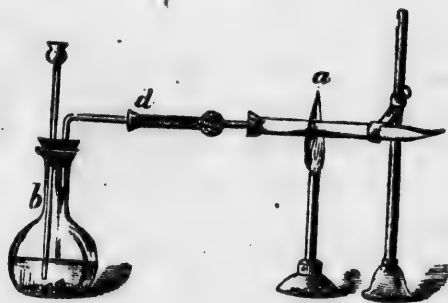
blackened, while the issuing gas does not become brown when mixed with air, but exhibits the properties of nitrogen when collected and examined. The oxygen is abstracted by the copper just as in the former experiment with potassium. If the copper be weighed before and after experiment, the gain in weight represents the oxygen derived from the nitric oxide ; and if the volume of the latter be known, we have but to find the *volume* that corresponds to the weight of oxygen abstracted ; this proves to be but *half* that of

the nitric oxide, hence the latter contains half its volume of nitrogen and half of oxygen.

The molecule of nitric oxide is therefore made up of one atom each of nitrogen and oxygen, and its specific gravity, 14·99, confirms this conclusion, for 14·99 × 2 = 29·98 is the molecular weight of the gas, or the weight of two *vols* in centigrams; now one *vol* we know to be nitrogen weighing 14 centigrams, and one *vol* oxygen weighing 16 centigrams, and 16 + 14 = 30. Therefore the formula of the gas is certainly NO.

But the nitrogen atom is pentad, or five-link, and that of oxygen diad, or two-link, and no possible combination of these single atoms can give us anything but an unsaturated molecule with one link unattached ; thus we have a remarkable exception to the general rule that free molecules have all their links (i.e., centres of attraction) of their component atoms engaged. Some chemists, in order to get over this difficulty, write the formula N_2O_2, assuming that the two *quasi* monad NO groups satisfy one another ; but this is, as we have seen, contrary to the molecular weight according to Avogadro's law. Curiously enough, nitrogen peroxide gas is also an exception, for its composition and specific gravity at temperatures far above its condensing point lead to the formula NO_2, which is irregular like NO, but when the gas is cooled down its specific gravity increases from 23 (H = 1) to nearly 46 when close to the condensing point—the latter number gives the molecular weight 92 and the formula N_2O_4. Thus the combination assumed in the case of nitric oxide can be distinctly

traced in that of nitrogen peroxide ; nevertheless, the simpler formula for each gas is that which best represents the composition at ordinary temperature and pressure.

It must be remembered, however, that the existence of exceptions such as those pointed out do not invalidate the general rule stated, but they serve to show that the law according to which 'links,' 'bonds,' or 'atomicities,' as they are variously called, disappear, is yet but imperfectly known.

NITROGEN MONOXIDE (*Nitrous oxide, or laughing gas*) = N_2O. 1 *Vol weighs* 21·99 *c.grs.* *Molecular weight* = 44.

FIG. 66.
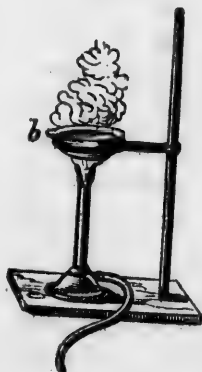
Experiment 110. — Pour some 30 or 40 c.cs. of strong nitric acid into an evaporating basin (see fig. 66) ; dilute with an equal volume of water, and add gradually the strong commercial 'solution of ammonia' until the acid is neutralised ; this point is ascertained by test-paper in the way already described. The liquid in the dish is now a solution of ammonium nitrate—

$$\underbrace{HNO_3}_{\substack{\text{Nitric} \\ \text{acid.}}} + \underbrace{NH_4OH}_{\substack{\text{'Solution of} \\ \text{ammonia.'}}} = \underbrace{NH_4NO_3}_{\substack{\text{Ammonium} \\ \text{nitrate.}}} + H_2O$$
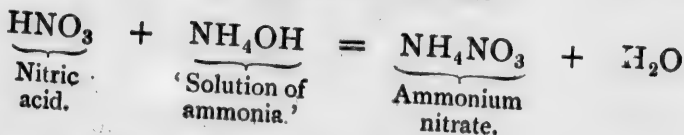
The nitrate is obtained in the solid state by evaporating the solution to dryness ; the residue

when cold, is removed from the basin and preserved in a well-closed bottle, as it is a deliquescent body.

Experiment 111.—Fit up a Florence flask as for the preparation of oxygen (fig. 67). Introduce into the flask about 30 grams of the ammonium nitrate, prepared as just described, and having inserted the cork carrying the delivery tube, and filled the pneumatic trough with *hot* water (*vide c*), apply heat. The salt melts, and evolves much gas and steam as the temperature reaches 230° C. The gas is termed

FIG. 67.
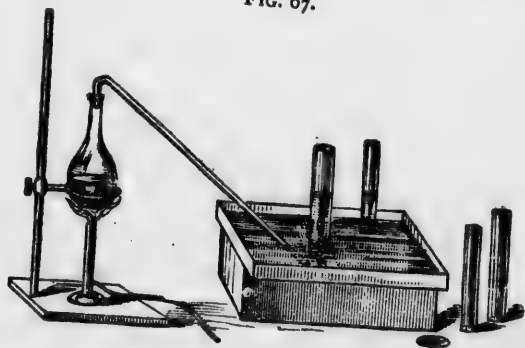
nitrous oxide; when its evolution commences the heat must be carefully applied, so as to avoid a too rapid and dangerous decomposition. Collect several jars of the gas, and at once remove the delivery tube from the water. The gas in the jars is generally cloudy at first, owing to particles of saline matter carried over in the current, but it soon becomes clear; note that it is colourless.

a. Remove a jar, and plunge into the gas a burning taper; its combustion is much more rapid than in air.

b. Into another jar of gas plunge burning phos·

phorus, carbon, wood, or sulphur, and note that nearly as vivid combustion ensues as in oxygen; but all the bodies, more especially sulphur, require to be burning strongly in air before they are brought into the gas, else they are extinguished.

c. Transfer a jar of gas to a vessel of cold water; allow about one-fourth of the gas to escape, then firmly close the mouth of the jar while under water with the hand, and shake up the gas with the water enclosed in the jar. The hand will be drawn against the mouth of the jar, and on bringing the latter under water and removing the hand the proportion of gas to water will be considerably reduced, indicating that some of the gas has dissolved. By repeating this treatment several times, the gas, if free from air, will be completely absorbed. Therefore this gas, unlike oxygen, is tolerably soluble in cold water; in fact, 1·00 c.c. of water at 15° C. dissolves 0·7778 c.c. of the gas,[1] but it does not dissolve in water near to the boiling point.

Experiment 112.—Heat some potassium in a tube of this gas, exactly as described for nitric oxide in Experiment 1c and note that the gas does not diminish in volume after evident decomposition by the metal, and the residual gas possesses the properties of pure nitrogen. Therefore the molecule of this gas, unlike that of nitric oxide, contains *its own volume of nitrogen.*

By the method adopted in Experiment 109 it can be shown that this gas, like nitric oxide, contains half

[1] 1·00 c.c. of alcohol at the same temperature absorbs 3·267 c.cs. of the gas.

its volume of oxygen. It therefore contains, for the same volume of oxygen, twice as much nitrogen as nitric oxide, and its formula is N_2O.

The change that takes place on heating ammonium nitrate is therefore represented by the equation—

$$\underbrace{NH_4NO_3}_{\substack{\text{Ammonium} \\ \text{nitrate.}}} = \underbrace{N_2O}_{\substack{\text{Nitrous} \\ \text{oxide.}}} + 2H_2O$$
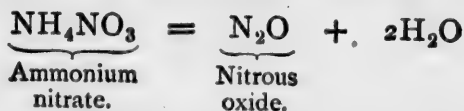
The molecular weight of the body should be $44 = (14 \times 2) + 16$, and its specific gravity $(H = 1)$ ought to be $\frac{44}{2} = 22$. The experimental number is $21 \cdot 99$; therefore the above formula is correct. Consequently 1 *vol* weighs $21 \cdot 99$ c.grs. at $0°$ C. and 760 m.ms.

Experiment 113.—Take a jar, that we may call A, containing only air, and hold it mouth upward. Take a jar, B, of N_2O, and turn it mouth upward also and remove its plate. Now slowly pour the gas from B into A, just as you would pour a liquid from the vessel, and test both jars with a taper having a glowing wick. The taper is re-kindled in A, but not in B, thus proving that the gas is so much heavier than air ($1 \cdot 52$ times) that it can displace the lighter air just like liquid. The gas cannot be retained in an open vessel for any length of time, as it escapes by diffusion (see Experiment 92) into the atmosphere. It is liquefied by a pressure of 30 atmospheres at $0°$ C.

The gas is often termed *laughing gas*, in allusion to the curious property Sir Humphry Davy found it to possess, when mixed with some air and inhaled, of causing temporary excitement and a sense of

exhilaration.   When unmixed with air or oxygen, and
pure,[1] nitrous oxide produces insensibility if inhaled
for a short time ; at first ringing noises are heard and a
'general sense of pulsation' is experienced, then sleep
supervenes, during which any short operation, such
as the extraction of a tooth, can be and frequently is
performed.   A few full respirations of pure air restore
the patient, and no unpleasant after-effects follow the
administration.   In the latter respect nitrous oxide
is superior to ether and chloroform as an anæsthetic
(i.e., a body used to procure insensibility to pain), but
the gas can completely suffocate if too long inhaled.
Ringer says of it : ' It appears to me to produce its
anæsthetic effect by preventing oxidation of the ner-
vous centres, and this chiefly by depriving the blood
of its supply of free oxygen from the air.'   Although
there is *more* oxygen in nitrous oxide than in air,[2]
it is chemically combined with nitrogen, and thus
we have, in the comparative action of nitrous oxide
gas and air on the animal economy, a remarkable illus-
tration of the wide difference in characters that may
exist between a chemical compound and a mechanical
mixture of the same elements.

    We have thus recognised the existence of five
oxides of nitrogen, two of which are anhydrides of
distinct acids.   If we assume that the molecule of

---

[1] Nitrous oxide gas intended for inhalation should be
purified from ammonia and higher oxides of nitrogen by
obliging it to pass in succession through sulphuric acid and
solution of ferrous sulphate, or green vitriol, contained in
suitable wash-bottles.

[2] 38·6 per cent. by weight, as against 23 per cent. in air.

each oxide contains the same weight (i.e., 28 parts) of nitrogen—although we know this is not quite true in one instance at least—it follows that the group of known oxides of nitrogen is a complete series of compounds resulting from successive additions of single oxygen atoms to the lowest term—i.e., nitrous oxide. Thus—

Nitrous oxide	.	.	.	N_2O
Nitric oxide .	.	.	.	N_2O_2, or NO.
Nitrogen sesquioxide, or nitrous anhydride .	.	.	.	N_2O_3
Nitrogen dioxide .	.	.	.	N_2O_4, or NO_2
Nitric anhydride .	.	.	.	N_2O_5.

In this group of bodies we therefore have additional evidence in support of the law of *multiple proportions* already deduced from the examination of the two oxides of hydrogen. (*Vide* Part I. under Experiment 80.)

AMMONIA $= NH_3$. 1 *Vol weighs* 8·5 *c.grs.*
Molecular weight $= 17$.

Experiment 114.—Boil some metallic zinc with strong caustic potash solution in a large test-tube; the metal slowly dissolves and a gas is evolved which burns at the mouth of the tube, and can be easily shown to be hydrogen, and *zinc potassate* is left—

$$Zn + 2KOH = Zn''(OK)_2 + 2H.$$
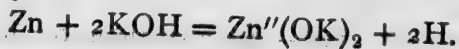
On the addition of a few drops of nitric acid or a little *nitre* to the solution and again heating, the pungent smell of *hartshorn* is noticed, and a piece of

red litmus paper held in the current of steam is rendered blue, proving the presence of an *alkaline* vapour. We may anticipate the results of some future experiments by stating that in this case a portion of the hydrogen, no longer set free, but when in the *nascent* [1] state, quickly deoxidises the nitre, forming therewith water, while another portion unites with the nitrogen of the nitre and forms *ammonia* gas, which latter is evolved, while potassium hydrate is left in solution. Thus—

$$\underbrace{KNO_3}_{\substack{\text{Potassium} \\ \text{nitrate.}}} + \underset{}{8H} = \underbrace{NH_3}_{\text{Ammonia.}} + \underbrace{KOH}_{\substack{\text{Potassium} \\ \text{hydrate.}}} + 2H_2O$$
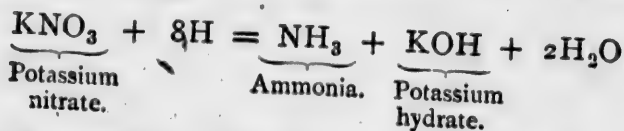
Experiment 115.––Pass a current of gaseous hydrogen through a hot alkaline solution of nitre, and test the issuing gas with reddened litmus-paper. No trace of alkaline ammonia can be detected if the materials employed are pure, and care be taken to prevent any of the liquid reaching the paper.

These two experiments well illustrate the difference in activity between the comparatively stable free molecule of hydrogen and the same element in the *nascent* condition—i.e., at the moment of liberation of its atom from a compound, and, as some suggest, before it can meet with another atom in order to form the gaseous molecule. Many other cases of a similar kind will be met with later on.

Experiment 116.—Take a tube of hard glass closed at one end, and one-third fill it with pieces of horn, bone, gelatine, feathers, wool, hair, or, if the

[1] From *nascor*, to be born.

tube be a large one, fragments of coal, and apply heat. The organic or carbonised matter soon decomposes under the influence of the heat, and various volatile and strongly smelling products are obtained, amongst which *ammonia* may be recognised by its power of changing the colour of red litmus-paper to blue. All the bodies mentioned agree in containing nitrogen—even coal contains from 1 to 2 per cent.—and, during the above process of *destructive distillation* [1] by heat, it combines with hydrogen, likewise present, and forms ammonia. All nitrogenised animal and vegetable bodies afford more or less ammonia in this way, not only at high but at ordinary temperatures, when they undergo slow putrefactive change or decomposition in presence of moisture—in fact, much of the atmospheric ammonia is derived from these sources.

FIG. 68.

Most of the ammonia employed in the arts is obtained from the tarry ammoniacal liquors collected during the manufacture of coal gas. The preparation of *sal-ammoniac* and similar compounds from these solutions will be referred to under 'Salts of Ammonia' in Part III.

Experiment 117.—Coarsely powder some *sal-ammoniac*, or ammonium chloride (NH_4Cl), and mix it with rather more than its own weight of slaked

[1] Or distillation attended by decomposition.

lime in fine powder, quickly transfer the mixture to the flask *f*, fig. 68, insert the cork carrying the delivery tube *d*, and invert over the free end of the latter the dry bottle *g*. On applying a very gentle heat to the mixture in *f*, abundance of ammonia gas is evolved, the pungent smell of which is quickly perceived, while red litmus-paper passed up into the gas is instantly turned blue, and white fumes are produced when a glass rod, moistened with hydrochloric or acetic acid, is brought to the mouth.[1] Note that the pure gas is colourless.

$$2NH_4Cl + Ca(OH)_2 = 2NH_3 + CaCl_2 + 2H_2O$$

Ammonium   Calcium   Ammonia.   Calcium
chloride.   hydrate.   chloride.
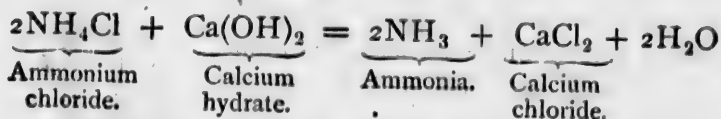
a. Pass up a lighted taper into a jar full of ammonia. The flame is extinguished without igniting the gas.

FIG. 69.

b. Take a dry gas jar and attach a piece of red litmus-paper near the top inside by means of gum. Invert the tube, and bring under its mouth a rather larger tube full of ammonia gas, as shown in fig. 69, and slowly invert the latter. The colour of the litmus in the upper jar quickly changes, proving the ascent of the ammonia, and the flame of a taper is extinguished if passed up into the gas. Therefore am-

[1] Any other ammoniacal salt may be used instead of the chloride, and potassium or sodium hydrate instead of lime.

monia is lighter than air, and displaces the latter from the upper jar. Its specific gravity is 8·5 ($H = 1$), or but little more than half (0·586 if air $= 1$) as heavy as air.

c. Fill another stout bottle with the gas, close with a glass plate, and remove, still mouth downwards, to some water; withdraw the plate when the mouth
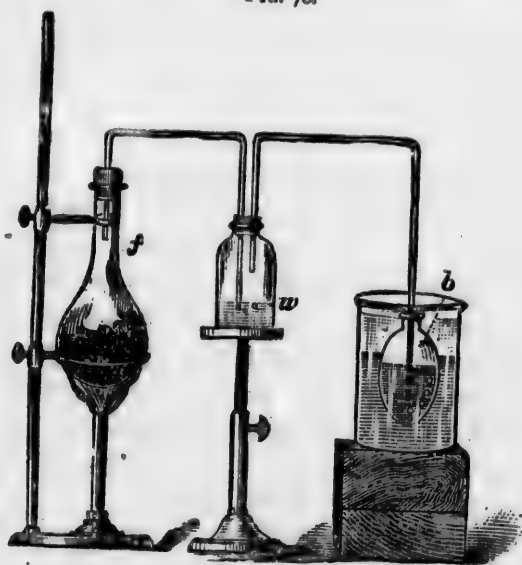
is under water. Note that the water rapidly rushes into the jar and nearly fills it; therefore ammonia gas is very soluble in water—in fact, 1 c.c. of water at 15° C. and 760 m.ms. dissolves 783 c.cs. of ammonia gas, or 783 times its volume.

Experiment 118.—Prepare ammonia gas as before, but wash it from impurity by making it pass

O

through the small quantity of water [1] in the little wash-bottle *w*, fig. 70, and then conduct the gas into a measured quantity of water contained in the bottle *b*, which latter is cooled by immersion in a beaker of cold water, as heat is evolved during absorption of the gas. Apply heat to the flask *f*, and pass the gas through the water in *b* as long as it is absorbed, but when bubbles pass through without sensibly diminishing in size it may be concluded that all the gas has been dissolved that the water can hold at the particular temperature and pressure. Measure the bulk of the liquid in *b* after the experiment, and it will be found to have increased to the extent of about one-half its volume. [2] This 'solution of ammonia' is colourless, with a characteristic and very pungent smell, and strong *alkaline* reaction to test-papers. The specific gravity of the solution is about 0·88 (water $=$ 1).

When the solution is heated, ammonia gas is expelled, and after boiling for a short time almost every trace of the gas is removed; thus 'solution of ammonia' is a very convenient source of the gas, and we shall use it presently for this purpose. Ammonia gas is also easily soluble in alcohol.

The extraordinary solubility of ammonia gas in water, accompanied as it is by considerable evolution of heat, is commonly regarded as due to true chemical combination—a new body being formed which closely

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[1] Rather more than 50 c.cs. of water should be used for every 100 grams of sal-ammoniac.

[2] The process employed on the large scale in the manufacture of '*liquor ammoniæ fortior*' of the British Pharmacopœia is identical with that given above.

resembles potassium and sodium hydrates in its highly alkaline character and power of neutralising acids (e.g. nitric acid, Experiment 110), and forming salts analogous to those of potassium and sodium ; hence the liquid may be fairly regarded as a hydrate similar to those of the metals above named, in which hydroxyl is united to a monad compound radicle NH$'_4$, which acts like a monad metal and is termed *ammonium*.[1] Thus—

$$\underbrace{NH_3}_{\text{Ammonia.}} + H_2O = \underbrace{NH'_4OH}_{\substack{\text{Ammonium} \\ \text{hydrate.}[2]}}$$
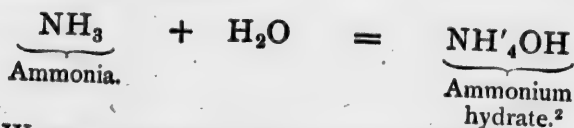
Water saturated with ammonia gas at 0° C., and under the pressure of 760 m.ms., may be regarded as nearly pure ammonium hydrate, since it contains a weight of ammonia equivalent to about 96 per cent. of NH_4OH. But a slight elevation of temperature suffices to decompose this body, and nearly all the gas can be expelled before the liquid reaches 100° C. Thus—

$$NH_4OH = NH_3 + H_2O.$$
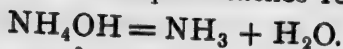
From the above experiments we learn how to prepare and to recognise ammonia gas, and to obtain 'solution of ammonia' of the British Pharmacopœia, or ammonium hydrate.

Ammonia can be condensed to a colourless liquid by cooling the gas to a temperature of − 40° C. or F.

[1] See further, Experiment 124.

[2] Another compound is known, which is intermediate in composition between NH_3 and NH_4OH ; its composition is represented by the formula NH_2OH, and it is called *hydroxylamine*, since in it one atom of the hydrogen of ammonia has been *replaced* by the group OH or hydroxyl.

(and, it may be stated, this particular temperature is the only one indicated by exactly the same value on the Centigrade and Fahrenheit thermometer scales) by means of a freezing mixture of two parts of snow and three parts of crystallised calcium chloride.

The comparative ease with which ammonia gas can be liquefied by cold leads to the presumption that it admits of liquefaction by very moderate compression at ordinary temperatures. By means of the following

FIG. 71.
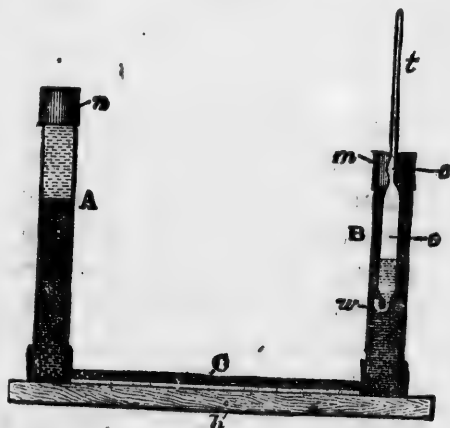
cheap and effective apparatus we can reduce the gas to the liquid form.

Experiment 119.—A species of U tube of stout wrought iron is made of the form shown in fig. 71, *A C B.* *A* is about 40 centimeters long, *B* 30 centimeters, and each is 2 centimeters internal diameter; *C* is about 25 centimeters and 5 or 6 millimeters internal diameter, and is securely screwed into the two wider tubes. The whole is fastened to the wooden stand *h.* *A* is provided with a stout screw-cap *n*, the joint

being rendered gas-tight by a leather washer. *B* is also fitted with a strong screw-cap with a deep head, through which a conical hole is bored ; the long glass tube *t* of the apparatus *t o* passes through this hole to the expansion *c*, which should fit into the cone and be there secured by any good cement. The screw-cap *m* therefore carries the glass apparatus, which latter is a form of pressure tube now easily obtained through good instrument-makers. The liquefaction is to take place within the glass tube *t*, which must of course be very strong ; the length of this tube is about 25 centimeters, and at first it is open ; the wide reservoir *o* must have at least ten times the capacity of *t* ; the reservoir *o* terminates below in a rather narrow curved tube *w*, which is always open. The glass apparatus must be filled with dry ammonia gas by connecting *w* by means of a flexible tube with *f*, fig. 70, affording a current of ammonia gas, but freed from moisture by passing through a long tube packed with fragments of fresh quicklime. When all air has been expelled— and a good current maintained for ten minutes is sufficient to effect this—the flow of gas is allowed to slacken and the capillary end of *t* securely sealed at the blowpipe ; the tube is removed from *w* and the latter at once dipped in mercury, which enters and prevents escape of ammonia.

Now remove the cap *n*, and pour mercury into *A* until the metal rises nearly to the top of *B* ; then introduce *o* into *B*, allowing the mercury displaced to overflow into a vessel placed to receive it, and screw home the cap *m* (which of course must be provided with a good leather washer). We have, therefore,

nothing but mercury between the gas in *o* and the surface of the metal in *A*.   Next remove enough mercury from *A* by a pipette to leave a space of some 12 centimeters between the surface of the metal and the cap ; then fill up to the top with the strongest 'solution of ammonia,' and screw down the cap *n*, and the apparatus is ready for experiment, which is performed in the following way :—

Gradually heat the portion of *A* containing the solution of ammonia by a Bunsen flame occasionally applied ; as the temperature rises, ammonia is expelled from the solution, but since the gas has no escape, considerable pressure is exerted in *A* on the surface of the mercury, and the latter, acting as a fluid piston, compresses the gas in *o*, which steadily diminishes in volume until at last the mercury rises into view in *t* ;[1] and if the heating of *A* be now carefully managed, the compression proceeds until a layer of colourless liquid is seen to form on the surface of the mercury in *t*.   This is the liquefied ammonia, and is obtained when the pressure reaches about 6·5 atmospheres at mean temperature.

If the joints are well made and the heating well managed, it is easy to maintain a steady pressure for a considerable time, but anything like violent heating must at all times be carefully avoided.   On allowing the apparatus to cool, the mercury recedes in *t*, and the liquefied ammonia disappears.   This apparatus is always ready for experiment, though it is desirable to

[1] It is well to cover *t* with a large cage of fine wire gauze, lest the glass should give way when first subjected to considerable pressure.

unscrew the cap of *A* occasionally and change the solution of ammonia, as slow leakage from *n* is inevitable.[1]

Experiment 120.—As we have already seen (Experiment 117, *a*) ammonia does not burn when a light is applied to the cold gas. Now pass it through a narrow glass tube heated to redness near to the point at which gas issues, and it can be easily ignited, burning with a greenish-yellow flame in the oxygen of the air; it produces nitrogen gas and *water*, hence a cold body introduced into the flame is quickly bedewed with moisture—

$$2NH_3 + 3O = 2N + 3H_2O.$$

Experiment 121.—A similar result is obtained if a stream of cold ammonia gas (obtained by heating some 'solution of ammonia') issuing from a jet be surrounded by oxygen gas and then ignited. The little apparatus, fig. 72, enables this experiment to be easily performed. *a* is a short brass tube into which oxygen gas can be admitted through the side tube *o*; *n* is a glass tube delivering ammonia; this passes through the cork *c*, which fits the brass tube *a*. Ammonia is allowed to flow through *n*, and then oxygen gas, derived from a bag or gas-holder, is turned on cautiously,

FIG. 72.
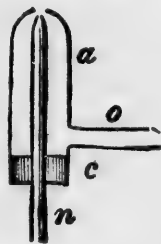
[1] As the use of a pressure pump is altogether avoided in this apparatus, it is inexpensive. Before using any form of apparatus for experiments of the kind described, it should be fully tested by the maker, and then should only be used by a careful manipulator.

while a flame is applied to the jet. When the proportions of the two gases are properly adjusted a tolerably steady flame can be obtained.[1]

If in the last two experiments, but more especially in Experiment 120, we dry the ammonia by passing the gas through a tube filled with fragments of *quicklime* (CaO), the appearance of water as a product of combustion is proof that hydrogen is a constituent of ammonia, while the mode of generating the latter from nitre adopted in Experiment 114 leaves little doubt that nitrogen is another constituent of the body; but the following experiment affords us complete evidence of the composition of ammonia.

Experiment 122.—Fill the eudiometer (fig. 73) one-fourth with say 20 c.cs. of dry ammonia gas over mercury. Measure the volume and pass a series of sparks from an induction coil between the wires within the tube.[2] The confined gas is thus intensely heated

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[1] In these experiments the rapid oxidation of ammonia involves complete decomposition; but when slowly oxidised, especially in aqueous solution, it first affords nitrous acid, thus—

$$NH_3 + 3O = HNO_2 + H_2O.$$
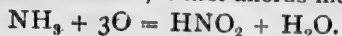
The nitrous acid then unites with another atom of oxygen, and produces nitric acid, thus—

$$HNO_2 + O = HNO_3.$$

The organic matter of sewage readily affords ammonia on decomposition, and the latter then undergoes slow oxidation as just stated; hence in sewage-contaminated water *nitrites* and *nitrates* are usually to be found.

[2] In this case a Leyden jar must be placed in circuit in order that the maximum heating effect may be obtained. For this purpose it is merely necessary that one of the coil wires should be in metallic connection with the knob, and the other with the external coating of the jar.

and decomposed, and if the sparks are passed for a sufficient time the volume of gas increases to 40 c.cs., or is *doubled.* Having obtained the maximum expansion, note the volume, and introduce 20 c.cs. of pure oxygen and explode in the usual way. After correcting for alteration of level, the residual gas will measure only 15 c.cs.; therefore 60 − 15 = 45 c.cs. of gas have disappeared, two-thirds of which, or 30 c.cs., must be hydrogen and the rest oxygen (see Experiment 24). As 20 c.cs. of oxygen were introduced, and 15 c.cs. have thus disappeared in union with hydrogen, the residual gas in the tube must contain 5 c.cs. of oxygen. This residue measures, as we have seen, 15 c.cs.; hence 15 − 5 = 10 c.cs. of nitrogen left.[1] To sum up, then, our experiment proves, firstly, that ammonia gas contains only nitrogen and hydrogen ; secondly, that it is completely decomposed into its constituents at a high temperature ; thirdly, that the resulting mixture of gases occupies twice the volume of the original ammonia ; fourthly, that this gaseous mixture contains one volume of nitrogen and three of hydrogen—consequently the molecule of am-

FIG. 73.

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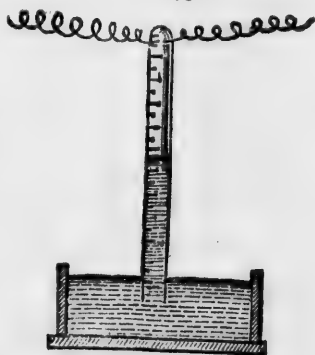
[1] By passing up a few drops of caustic potash, followed by a strong solution of pyrogallic acid (see Experiment 83), the oxygen is absorbed and nitrogen only is left in such a condition that it can be easily identified.

monia gas contains one atom of nitrogen and three atoms of hydrogen, and must be represented by the formula NH_3,[1] and its molecular weight by 17

FIG. 74.

(14 + 3). This result is confirmed by the specific gravity of the gas, which, as we have already seen (page 49), is 8·5, and 8·5 × 2 = 17. 1 *vol* of ammonia gas (112 c.cs. at 0° C. and 760 m.ms.) weighs 8·5 c.grms

Experiment 123.—Pour a few drops of strong commercial hydrochloric or 'muriatic acid' into a wide-mouthed bottle ; cover with a glass plate and turn the bottle about so as to distribute the acid over the sides. Fill another bottle with ammonia gas, bring its mouth down on the glass plate that covers the first, as shown in fig. 74, and then remove the plate from between them so as to leave them mouth to mouth. White fumes are instantly formed in abundance, and they deposit a white saline body on the glass after a time which is

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[1] We can recognise the nitrogen acting as a one-link, or monad atom, in nitrous oxide, $N'—O''—N'$, or N_2O ; as a three-link, or triad, in ammonia, $N'''H'_3$, and as a five-link, or pentad, in ammonium hydrate, $N^vH'_4(OH)'$, the monad group hydroxyl, OH', satisfying the fifth link. In the case of sal-ammoniac, $N^vH'_4Cl'$, we also have evidence of the five-link or pentad character of the nitrogen atom. In all these cases the links or bonds appear or disappear in pairs.

identical wlth sal-ammoniac or ammonium chloride, for

$$\underbrace{NH_3}_{\text{Ammonia.}} + \underbrace{HCl}_{\substack{\text{Hydrochloric} \\ \text{acid.}}} = \underbrace{NH'_4Cl}_{\substack{\text{Ammonium} \\ \text{chloride.}}}$$
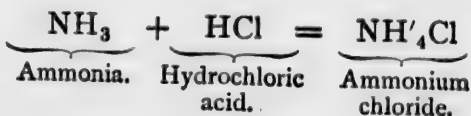
Thus at the commencement of our experiments we decomposed or *analysed* sal-ammoniac, and now we have reformed it or effected its *synthesis*, and we have written the formula of the body in such a way as to indicate that it is the chloride of the compound radicle ammonium NH'_4, already referred to under Experiment 118, rather than NH_3HCl, the formula directly justified by its mode of formation. Now the former view assigns to the group NH'_4 a pseudo-metallic character, and it may be fairly asked whether ammonium has been isolated, and, if so, whether it presents any of the metallic characters. As a matter of fact, ammonium, NH'_4, is not known in the *free* state, but a curious body can be prepared which is supposed to be a solution of ammonium in mercury. This body is easily obtained in the following way.

Experiment 124.—Introduce about one cubic centimeter of mercury into a wide test-tube; gently warm the metal over a lamp and, directing the mouth of the tube away from the person, drop in a fragment of clean metallic *sodium* about half the size of a pea. If the mercury be warm enough, the sodium will at once dissolve in it with a little explosion—if not, heat gently. Then introduce another piece of sodium of the same size, and after its solution a third. A silvery white *amalgam* of sodium is thus prepared

which retains the metallic lustre.[1] Now pour out the warm and still liquid amalgam (for if allowed to become cold it will become pasty or solidify) into about 250 c.cs. of a cold saturated solution of sal-ammoniac (see Experiment 73). The amalgam quickly increases to at least 15 times its original bulk, and ultimately becomes a large pasty mass, light enough to *float* on the surface of the liquid. This mass can be removed and washed with water ; it presents a brilliant metallic appearance, but it is very unstable and soon decomposes, evolving ammonia and hydrogen gases, and after some time nothing remains but the original mercury. This body appears to be a true amalgam of mercury and the metal-like ammonium, the latter taking the place of the sodium ; thus—

$$\underbrace{Hg_x Na}_{\substack{\text{Sodium}\\ \text{amalgam.}}} + NH_4Cl = \underbrace{Hg_x NH_4}_{\substack{\text{Ammonium}\\ \text{amalgam.}}} + NaCl$$
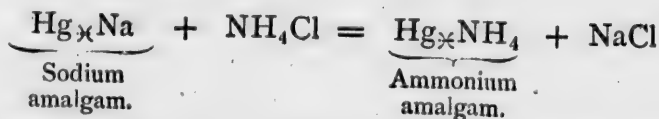
The amalgam then breaks up in the following way—

$$Hg_x NH_4 = Hg_x + NH_3 + H.$$

There is therefore some experimental evidence as to the existence of the compound metal ammonium, and the close analogies traceable between its saline and other compounds and those of potassium and sodium confirm this view; but it would lead us too far out of our course to examine this question here ;

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[1] Alloys of metals with mercury are termed *amalgams* ; in some cases these are mere mixtures of metals, in others feeble chemical union takes place, but the product in all cases retains the metallic appearance.

hence we·shall reserve this part of our study until we have to deal with the compounds of the alkali metals in Part III.

Experiment 125. – Powder half a gram or so of iodine and add it with frequent stirring to 20 c.cs. of ammonium hydrate solution ; allow it to stand for half an hour until a black powder has completely subsided, then pour away the clear liquid and distribute the black residue on pieces of bibulous paper. Put these in some safe airy place to dry. When the black substance is dry, a touch suffices to make it *explode*, when violet vapours of iodine are evolved. If small quantities are operated upon and reasonable care exercised, the experiment is not attended with danger.

The black substance is called *iodide of nitrogen*, and is really a mixture of ammonia derivatives. Dr. Gladstone's formula for the chief substance is NHI_2, or ammonia in which two-thirds of the hydrogen has been replaced by iodine. Analogous bodies are produced by the action of chlorine (chloride of nitrogen) and of bromine (bromide of nitrogen) ; but these are amongst the most dangerous explosives known, and have caused so many serious accidents that any description of their preparation is undesirable.

Many other derivatives of ammonia are known in which various groups of elements replace one or more atoms of hydrogen in NH_3 ; these will be met with later on in our course, but we may here give the formulæ of three of these important bodies—

Ethylamine.	Diethylamine.	Triethylamine.
$NH_2(C_2H_5)'$,	$NH(C_2H_5)'_2$	$N(C_2H_5)'_3.$
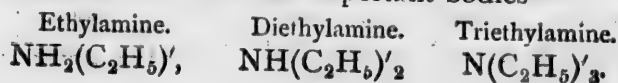
CHAPTER XV.

EXPERIMENTS WITH HYDROCHLORIC ACID AND CHLORINE.

HYDROCHLORIC ACID (*Muriatic acid*) = HCl. 1 *Vol of gas weighs* 18·19 *c.grs. Molecular weight* = 36·5.

Experiment 126.—Mix some sal-ammoniac—ammonium chloride, as we shall term it for the future—with strong sulphuric acid in a test-tube. Even without heat a quantity of gas is evolved which has a very pungent smell and fumes in the air ; it does not burn or support combustion of a match, but it *reddens* blue litmus-paper, and produces white clouds if a rod moistened with ammonium hydrate be brought near the mouth of the tube.

The gas evolved is therefore an *acid* gas capable of uniting with the alkaline ammonia, and this body is termed *hydrochloric acid*, and its symbol is HCl. Thus, in Experiment 117, we liberated ammonia gas from NH$_4$Cl, and in Experiment 123 re-formed the latter by effecting the combination of ammonia ·with hydrochloric acid. We have now broken up the compound again, but in such a way as to make it yield its acid constituent ; thus—

$$2NH_4Cl + H_2SO_4 = (NH_4)_2SO_4 + 2HCl$$

| Ammonium chloride. | Sulphuric acid. | Ammonium sulphate. | Hydrochloric acid. |
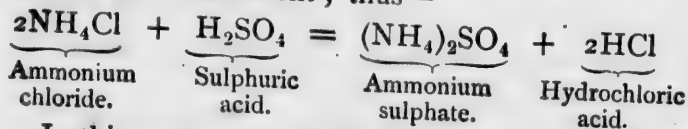
In this case, each group, NH$_4$, takes the place in

the sulphuric acid of one atom of H, and the latter
unites with the Cl of the ammonium salt and forms the
acid. The specific gravity of hydrochloric acid gas,
determined as in Experiment 27, is 18·19 (H = 1);
and 1 *vol* weighs 18·19 c.grms. Its molecular weight
is therefore 36·5 (if Cl = 35·5).

Experiment 127.—Make a similar experiment
with common salt or sodium chloride, and note that
the same acid gas is evolved. In this case

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl$$

Sodium chloride.   Sodium sulphate.
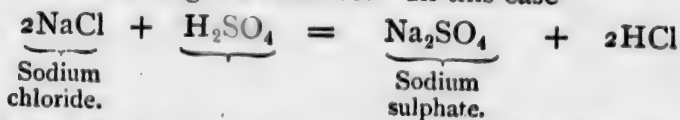
Lower the test tube from which HCl gas *freely* issues
into a small dry gas jar standing mouth upwards, and
loosely cover with a glass plate. After a minute or
two slip aside the glass plate, rapidly remove the test-
tube, and pour in a few cubic centimeters of water;
cover the mouth with the hand and shake up. Note
that a vacuum is produced, as evidenced by suction
of the hand, indicating that the gas has been absorbed
by the water; now test the latter with blue litmus-
paper and note that it has acquired an acid reaction.
Therefore hydrochloric acid gas is soluble in water and
produces an acid liquid. As a matter of fact, the gas
is very soluble in cold water, as we shall find presently,
for 1 c.c. of water at 15° dissolves 450 c.cs. of the
gas at the same temperature. It is a strong solu-
tion of the gas in water that constitutes the liquid
hydrochloric acid ('muriatic acid' or 'spirit of salt')
of commerce.

Experiment 128.—A glass flask, *f*, fig. 75, is
provided with a cork through which passes the gas

delivery tube bent twice at a right angle and passed
to the bottom of the wash-bottle *w*, which contains a
very little water, which a tube leads from *w* into a bottle
b containing cold distilled water. Place about 50
grams of common salt or sodium chloride in *f* and 50
c.cs. of water in *b*, and connect the apparatus as shown.
Measure 50 c.cs. of oil of vitriol and add it gradually

FIG. 75.
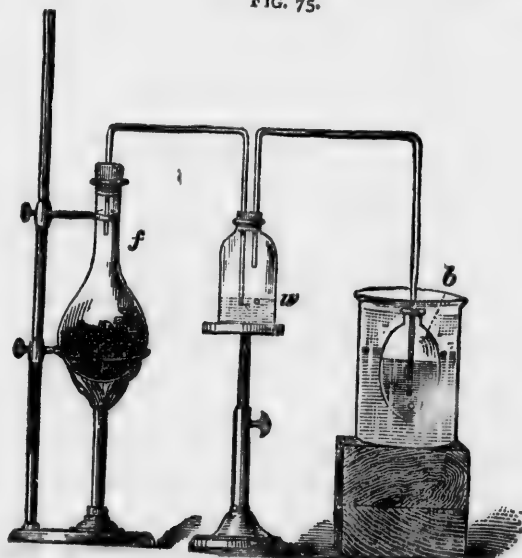
and with stirring *to* an equal volume of water contained
in a porcelain dish ; when cool, pour into the flask,
and then, if necessary, apply a gentle heat to *f*. HCl
is freely evolved as a *colourless* gas and passes through
the water in *w*, where the first portions are absorbed,
and then into the water in *b*. When all air has been
expelled from the solution, the bubbles that pass into
the water disappear before they reach the surface, the

gas is so easily soluble in water ; but when the latter is saturated they pass through without apparent diminution of bulk, and thus the end of the process can be recognised. The bottle *b* must be kept cool throughout, resting in the beaker of cold water.[1]

When the gas is being freely evolved it is well to remove the delivery tube from *b*, dry it, and pass it to the bottom of a gas jar placed mouth upwards and partially covered with a glass plate. When the jar is judged to be full of the gas, remove the tube, close the mouth and bring it under water. The latter quickly rushes up and almost fills the jar, or quite fills it if all air has been expelled.

The solution ultimately obtained in the bottle *b* is a nearly colourless and strongly acid liquid, emitting white fumes which have a pungent smell. Its specific gravity is about $1\cdot16$ (water $= 1\cdot0$), and it contains about 32 per cent. by weight of actual HCl. When heated this acid loses gas until the percentage of HCl is reduced to $20\cdot24$, and a solution of this strength boils at a constant temperature of $110°$ C. if the pressure does not vary from the normal (760 m.m).

The common 'muriatic acid' of the shops always has a yellow colour, owing to the presence of *iron*; other impurities commonly present are free chlorine, arsenic and sulphur compounds. Appropriate tests for these impurities will be found under their respective heads.

[1] The process given above is that directed by the British Pharmacopœia for the preparation of the pure acid. The crude commercial acid is chiefly obtained as a by-product in the manufacture of 'salt-cake,' or crude *sodium sulphate*. See Part III. p. 283.

Experiment 129.—Mix a few drops of the colourless acid prepared as above with ten or twelve parts of water, and add to the diluted acid a few drops of *silver nitrate* solution. Note that a white precipitate is produced that becomes curdy on shaking. Let the precipitate subside, pour off most of the liquid and then divide the precipitate between two test-tubes.

a. To one portion add some moderately strong nitric acid and boil. Note that the precipitate does not dissolve.

b. To the other part add NH_4OH solution; the precipitate soon dissolves completely, and can be reprecipitated when the ammonia is neutralised by nitric acid.

The precipitate possessing these characters is silver chloride, which is formed when silver nitrate is added to free HCl, or to *any soluble chloride* such as ammonium or sodium chlorides—

$$\underbrace{HCl}_{\substack{\text{Hydrochloric}\\\text{acid.}}} + \underbrace{AgNO_3}_{\substack{\text{Silver}\\\text{nitrate.}}} = \underbrace{AgCl}_{\substack{\text{Silver}\\\text{chloride.}}} + \underbrace{HNO_3}_{\substack{\text{Nitric}\\\text{acid.}}}$$
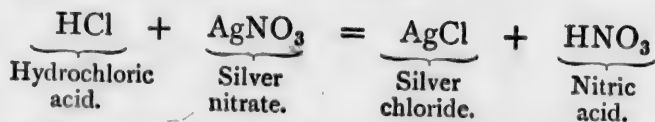
Experiment 130.—Add a few drops of solution of lead nitrate $(Pb(NO_3)_2)$ to some diluted hydrochloric acid; a white precipitate is obtained if the liquids are not very weak, and the body dissolves to a considerable extent in boiling water and separates out in white crystals on cooling the solution. This body is lead chloride, thus formed—

$$\underbrace{Pb''(NO_3)'_2}_{\substack{\text{Lead}\\\text{nitrate.}}} + 2HCl = \underbrace{PbCl_2}_{\substack{\text{Lead}\\\text{chloride.}}} + 2HNO_3$$
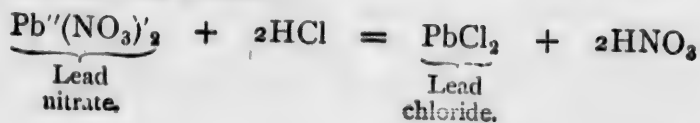
For another useful test of hydrochloric acid or a chloride, see Experiment 137 ; and for the distinction of the acid from free chlorine, see Experiment 147.

Experiment 131.–Dilute some strong hydrochloric acid with water, and add caustic soda until the acid is neutralised, as in Experiment 42. The solution contains sodium chloride, or common salt, and affords crystals of the compound on evaporation—

$$HCl + NaOH = NaCl + H_2O.$$
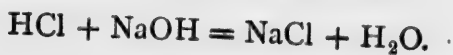
Other metallic hydrates afford corresponding chlorides when used to neutralise the acid.

Experiment 132.—Add some black oxide of copper to a little of the acid in a test-tube ; the oxide dissolves easily and forms a green-coloured solution which contains copper chloride—

$$Cu''O + 2HCl = Cu''Cl_2 + 2H_2O.$$
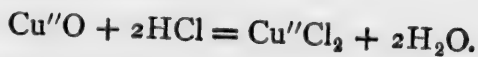
Other basic oxides are acted upon in a similar way by hydrochloric acid, and produce metallic chlorides and water ; but certain peroxides, such as MnO_2, give chlorine in addition (see Experiment 137).

Experiment 133.—Plunge a strip of zinc into some of the diluted acid in a test-tube. Brisk effervescence takes place, and the gas evolved burns when a flame is applied to the mouth of the tube. The gas is hydrogen resulting from the reaction—

$$Zn'' + 2H'Cl' = \underbrace{Zn''Cl'_2}_{\text{Zinc chloride.}} + 2H$$
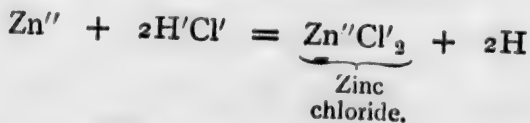
If iron be used instead of zinc, hydrogen is also

P 2

evolved, but ferrous chloride (*ferrum*=iron) is obtained in solution—

$$Fe'' + 2HCl = \underbrace{Fe''Cl_2}_{\substack{\text{Ferrous} \\ \text{chloride.}}} + 2H$$
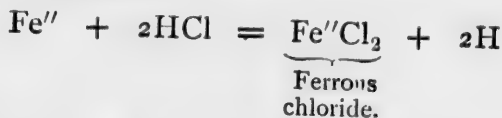
In each case the solid salt can be obtained by evaporation of the solution; for details, however, see the respective metals in Part III.

Experiment 134.—Take two test-tubes, pour into one 3 c.cs. of strong nitric acid, and into the other 4 c.cs. of strong hydrochloric acid. Put into each acid some pieces of *gold-leaf* and apply heat. Neither acid is able to dissolve the gold, or 'royal metal'; but on mixing the contents of the test-tubes the particles of gold disappear almost immediately; hence the mixture of acids is called *aqua regia*, because it alone dissolves gold or platinum, which latter is also classed as a noble metal.

When the two *strong* acids react, particularly on heating or long standing, the following products are obtained—

$$3HCl + HNO_3 = \underbrace{2Cl}_{\text{Chlorine.}} + \underbrace{NOCl}_{\substack{\text{Nitrosyl-} \\ \text{chloride.}}} + 2H_2O$$
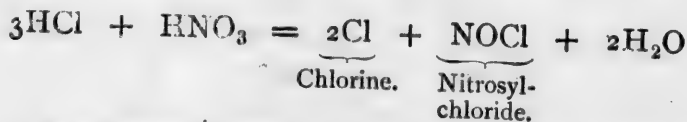
The solution of the gold (or platinum) is due to the action of the *chlorine* on the metal—

$$Au''' + 3Cl' = Au'''Cl'_3.$$
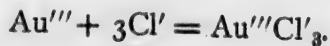
The *diluted nitro-hydrochloric acid* (B. P.) is prepared by mixing the strong acids in the above proportion (3 : 4), standing for twenty-four hours to permit nearly

complete change, and then diluting with 25 parts of water.

In order to avoid undue repetition we have hitherto assumed the formula HCl for the gas evolved when sal-ammoniac or when common salt is heated with sulphuric acid. We must now examine this body more closely.

Experiment 135.—We already know that sodium and chlorine are united in common salt. We shall now use the metal to remove chlorine from hydrochloric acid gas. Fill the U tube, fig. 76, with hydrochloric acid by passing a rapid current of the gas through it for some time; then close the stopcock *s* and immediately pour sufficient mercury into the open limb to close the bend *b*, and partially fill the tube as shown. Now adjust the level of mercury by opening the stopcock for an instant, as the gas must be under a little pressure, then mark the position of the mercury in the closed limb and fill up *o* completely with mercury containing some sodium amalgam, prepared as in Experiment 124. Next grasp *o* firmly in the hand, pressing the thumb on the opening and inclining the tube, make the gas go back and forward twice or three times through the mercury containing the sodium, at last transferring all the gas to the closed limb. Now remove the thumb and note that the mercury sinks in *o*; adjust the level of the mercury this time by adding to or removing the metal from *o*, and note that the gas in the closed limb occupies only *half* the volume of the hydro-

FIG. 76.

chloric acid. Fill up *o* with plain mercury, bring a
flame near to the jet, and cautiously open *s*—the re-
sidual gas rushes out and burns for an instant. This
is the hydrogen of which we have now proved hydro-
chloric acid gas to contain half its volume by Dr.
Hofmann's method.

Experiment 136.—Bend a tube in U form as in
fig. 77, and introduce some strong colourless solution
of hydrochloric acid. Next twist one of the bright
terminal wires of a small Grove's battery round a
carbon stick of the kind used in the electric lamp,
and the second wire round another carbon stick.

FIG. 77.

Now plunge the carbon poles[1] into the acid in the U
tube as shown. Gas is evolved at each pole—colour-
less and abundant at that connected with the zinc
side of the battery, less freely at first and coloured
from the opposite pole. The colourless gas can be
inflamed, and is easily proved to be the hydrogen of
the acid; the gas evolved at the positive pole has a
distinct greenish-yellow colour, a very irritating smell,
and neither burns nor rekindles a match with a glow-
ing tip; if, however, a piece of moistened blue litmus-
paper be laid over the mouth of the tube it is soon

[1] Carbon poles must be used, because platinum would be
attacked by the chlorine evolved during electrolysis of the
acid.

bleached a nearly pure white. This gas is an elementary body and has received the name of *chlorine*,[1] in allusion to its greenish-yellow colour ; its symbol is Cl and atomic weight 35·5. The volumes of the two gases evolved during electrolysis are approximately equal when the liquid becomes saturated with chlorine. The specific gravity of chlorine gas, determined as in Experiment 27, is 35·38 (H = 1), therefore 1 *vol* (=112 c.cs.) weighs 35·38 c.grs.

We know already (see page 63) that the molecular weight of hydrochloric acid gas deduced from its specific gravity is 36·5 ; and Experiment 135 proved that the molecule, as represented by 2 *vols*, contains 1 *vol*, i.e. one atom, of hydrogen, whose weight is 1 c.gr. Now, since 36·5 — 1 = 35·5, or almost exactly the weight of 1 *vol* of chlorine, we conclude that the molecule of hydrochloric acid gas consists only of hydrogen and chlorine, and of both chemically combined without condensation. Although this proof is complete, it is well to confirm the conclusion by direct synthesis ; before doing so, however, we must endeavour to obtain larger quantities of chlorine in a pure state and study the characters of that element. (For synthesis see page 219.)

CHLORINE – Cl.= 35·5. 1 *Vol weighs* 35·36 *c.grs. Molecular weight* = 71·0.—It is obvious that hydrochloric acid ought to afford an abundant supply of chlorine if we can remove its hydrogen and avoid

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[1] From χλωρός, in allusion to its colour. Chlorine is only met with in nature in combination, chiefly with sodium in common salt.

presenting at the same time a body that can combine with all the chlorine. Experiment 132 proves to us that a *monoxide* like copper oxide will not suit our purpose, since the metal can unite with all the chlorine displaced by the oxygen, but if we use a peroxide of a metal whose atom requires but two of chlorine to satisfy it, the excess of chlorine should be obtained in the free state. We shall, therefore, make the following experiment with a body of the kind referred to that we have already used, viz., manganese peroxide.

Experiment 137.—Heat a little manganese peroxide (MnO_2) in a test-tube with strong hydrochloric acid ; note that a greenish-yellow gas of suffocating odour is evolved which rapidly bleaches moist litmus-paper laid over the mouth of the tube. The gas is chlorine, resulting from the following change—

$$Mn^{IV}O''_2 + 4H'Cl' = Mn''Cl'_2 + 2Cl' + 2H_2O.[1]$$

The manganese chloride ($MnCl_2$) remains in solution.

Experiment 138.—Mix a little manganese dioxide with common salt and sulphuric acid in a test-tube and note that chlorine is evolved. In this case HCl is first formed by the action of sulphuric acid on common salt, as in Experiment 127 ; the hydrochloric acid then acts as above on the manganese dioxide.

Experiment 139.—Fit a Florence flask with a delivery tube bent twice at right angles, as shown

[1] According to Dumas, $MnCl_4$ is first formed and then decomposed by heat into free chlorine and manganese dichloride.

in fig. 78. Introduce into the flask about 20 grams of MnO_2 in lumps, and 100 c.cs. of crude but strong hydrochloric acid solution, and apply a *gentle* heat. Chlorine gas is so much heavier than air[1] that it can be easily collected by displacement of air as shown, the colour of the gas enabling the experimentalist to observe the rate of filling. As each jar fills, remove it and at once cover with a glass plate slightly greased so as to enclose the gas securely. Fill several jars in this manner, and make the following additional experiments, which, as

FIG. 78.

well as the generation of the gas, should be conducted near to a good draught, as the inhalation of chlorine is attended with danger, owing to the irritant action of the gas on the delicate tissues of the lungs.
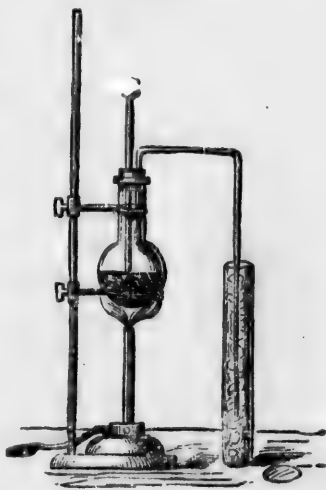
Experiment 140.—Plunge a burning wax taper into a jar of the gas (see fig. 79). Note that while combustion continues its character alters, for the flame is dull reddish, and much black smoke arises from it, acid fumes being freely produced. The latter

[1] As already stated (p. 215), it is $35\cdot5$ heavier than hydrogen, and, since air is $14\cdot47$ times heavier than hydrogen, it follows that chlorine is almost $2\frac{1}{2}$ times heavier than the same volume of air.

consist chiefly of HCl gas ; and the study of the change leads to the conclusion that the combustion in chlorine is due to the rapid chemical union of the latter with the hydrogen of the wax (a compound of hydrogen, carbon, and a little oxygen), but the carbon does not unite directly with chlorine, and therefore most of it separates, and in the finely-divided state of black smoke or soot. The attraction of hydrogen for chlorine must therefore be very great ; but the following experiment illustrates this important point still more clearly.

FIG. 79.

Experiment 141.—Moisten a strip of blotting-paper with a few drops of *turpentine* ($C_{10}H_{16}$), previously warmed, and, holding the paper by tongs, plunge it into a jar of chlorine. Spontaneous combustion soon takes place, and torrents of black smoke and acid vapour are evolved as before.

Experiment 142.—Take a strong and well-filled jar of chlorine, and another of the same size full of hydrogen gas. Bring them mouth to mouth, and, keeping them close together, invert several times so as to mix thoroughly, then separate and cover with glass plates. The mixture has a yellowish colour. Remove the cover from one of the jars and apply a flame ; an explosion results, and acid fumes of HCl are produced. Bring the second jar, which should be very securely closed by a well-greased ground

glass plate, into diffused daylight, but not into direct sunlight.[1] Note that the yellow colour slowly dis-appears, and when the contents have become quite colourless, carry the jar to the mercury trough, bring the mouth under the mercury, then remove the plate and note that the gas has not changed in volume, as gas does not escape, neither does mercury enter to any extent. Now pass up a few drops of water by means of a curved pipette, and note that the mercury now rises in the tube and will completely fill it if the original gases were pure and mixed in equal volumes. We have thus effected the synthesis of hydrochloric acid referred to under Experiment 136, and equal volumes have united without change of bulk, and the fact of their union is proved by the solution of the product in a small quantity of water, by which a mere mixture of hydrogen and chlorine would be very slightly affected. Synthesis therefore completely confirms the conclusion drawn from the analytical data.

In these cases

$$H + Cl = HCl.$$
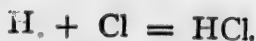
Experiment 143.—Plunge a small piece of dry phosphorus into a jar of Cl, using the long spoon

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[1] If the tube were exposed to direct sunlight, almost instant combination of Cl and H would have taken place with explosion. Small and thin glass bulbs are sold ready filled with the mixture of gases, and when exposed to direct sunlight (or to the light emitted by burning magnesium, which is also rich in chemically active violet and ultra-violet rays) the bulb is shattered to fragments, owing to the sudden expansion of the contents by the heat evolved on the combination of the two gases.

for the purpose. The phosphorus soon takes fire in the gas, and produces a mixture of chlorides of phosphorus, PCl_3 and PCl_5.

Cl can also be made to unite with sulphur, though heat is necessary, but it does not *directly* combine with either oxygen or carbon, though compounds with these elements can be obtained by indirect means.

Experiment 144. —Powder some metallic antimony very finely, and shake the powder into a jar of Cl. As the particles of metal fall through the gas, they burn, evolving much light and producing a most irritating vapour of antimony trichloride—

$$Sb''' + 3Cl' = Sb'''Cl'_3.$$
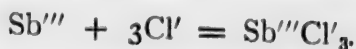
Chlorine acts upon *arsenic* with equal energy, and, when aided by heat, on all the true metals also, forming therewith chlorides, in which it acts as a single-link or monad element.

Experiment 145. —Write across the printed matter on a piece of newspaper a word or two in black writing ink, and plunge the paper into a jar of Cl. After a short time the writing ink, whose colour is due to gallo-tannate of iron, will be bleached, while the printing ink is unaffected, as the colouring matter of the latter is finely-divided solid carbon, which is not attacked by chlorine. Chlorine is therefore not an universal bleaching agent.

Experiment 146. —Remove a jar of dry gas to the pneumatic trough, and, having allowed some water to enter, close the mouth with the hand and shake up the gas and water ; the hand is drawn in, proving

that absorption has taken place, and on removing the hand under water the latter rises in the jar—therefore Cl is moderately soluble in water. 1 c.c. of water at 15° dissolves 2·368 c.cs. of Cl gas. Such a saturated solution of Cl in water forms the *Liquor Chlori* of the British Pharmacopœia, and is easily obtained by passing chlorine gas evolved from hydrochloric acid and manganese peroxide through a little water in a wash-bottle (as in fig. 75), and then through distilled water, until gas ceases to be absorbed. A liquid is thus obtained which rapidly bleaches indigo solution, writing ink, &c., and possesses the characteristic odour of the gas. If this solution be cooled by surrounding the bottle that contains it with melting ice, fine white crystals slowly separate which, when drained from the liquid in which they are formed and analysed, are found to consist of $Cl'5H_2O$. Very slight rise of temperature suffices to decompose this body into chlorine gas and water. Faraday first succeeded in obtaining liquid chlorine by sealing up some of these crystals in a strong glass tube and melting the solid, when two layers of liquid were obtained, the lower and heavier consisting of liquefied chlorine, the lighter of a solution of chlorine in water.

Experiment 147.—Take two test-tubes half full of distilled water, add to one a few drops of the solution of chlorine, and to the other a similar quantity of diluted hydrochloric acid. Now add to each a little silver nitrate solution and note that a similar white precipitate is produced in each case. Repeat the experiment with fresh solutions, but add potassium iodide instead of silver nitrate and note that no

change follows its addition to the hydrochloric acid, while a strong brownish yellow colour is developed in the free chlorine solution, and a black precipitate if the solutions are strong. This change is due to the separation of iodine (see Experiment 159), and serves at once to distinguish free chlorine from pure hydrochloric acid.

FIG. 80.

Experiment 148.—Take a tube of the form shown in fig. 80 and quite fill it with solution of chlorine;[1] now expose it to strong sunlight and observe that bubbles of gas are evolved and collect in the top of the tube, while the liquid gradually loses its yellow colour. Note that the liquid acquires a strong acid reaction. Since we have only chlorine and water present, and a colourless gas is separated, there is a strong presumption in favour of the gas being oxygen liberated from the water by the superior attraction of chlorine for hydrogen, and in accordance with the equation—

$$2Cl + H_2O = 2HCl + O.$$

We have already found the acid ; we now test the gas by filling up the little side tube with water, if it be not already quite full. then closing the mouth with a finger and so inclining the tube as to oblige the gas collected to pass into the small limb. Then have a match ready with a glowing tip, remove the finger and

[1] In this experiment the chlorine solution could not be confined in a tube over mercury, as the latter is quickly attacked by free chlorine.

test the gas, when the wood will be rekindled and the presence of oxygen ascertained.

In the absence of light the same change can be effected by passing a mixture of chlorine and steam through a red-hot porcelain tube.[1]

The ease with which chlorine decomposes water and sets free the oxygen leads us to enquire whether water plays any part in the bleaching action of free chlorine.

Experiment 149.—Take two perfectly dry stoppered bottles, warm them and fill each with chlorine by displacement of air, but dry the gas before it reaches the bottles by making it slowly bubble through some strong oil of vitriol. Now place in each bottle a strip of red flannel (madder-dyed) previously dried thoroughly by heat, insert the stopper and expose the flannel to the action of the chlorine for half an hour. If proper care was taken to exclude moisture, no material bleaching effect will be observed. Now introduce a few drops of water into one of the bottles, and the colour of the flannel will slowly fade while the dyed stuff in the dry chlorine will retain its colour. In this case, then, the bleaching effect of chlorine is indirect, and due to the powerful action of the *nascent* oxygen (see page 190, and note) derived from water; and similar experiments have shown that in most cases the presence of water is necessary, though we shall meet later on with some exceptions to this rule.

[1] We infer from these facts that chlorine does not tend to unite with oxygen directly, and it is not known to do so; nevertheless many oxygen compounds of the element are obtainable by indirect means (see Experiments 151 *et seq.*)

Chlorine is used in enormous quantities as a bleaching agent, but neither the free gas nor its solution in water are now employed for the purpose, as it is more convenient in practice to liberate the body from 'bleaching lime' and analogous compounds in contact with the materials to be bleached (see Experiments 151 and 152).

Experiment 150.—Introduce a few drops of *ammonium sulphide*—a yellow liquid of very offensive smell—into a bottle and gradually add chlorine water to it with agitation. Note that the unpleasant odour disappears, and the smell of chlorine is not detected unless too much of the latter has been added. In this case, then, the free chlorine acts as a *deodorant*, and it is commonly used for removing unpleasant smells, for which purpose a small quantity is generally sufficient. It is, moreover, believed to act as a *disinfectant*, either by direct corrosion of disease-particles or by its indirect oxidising action, though it is improbable that it usually produces much effect unless employed in large quantities. The most convenient source of chlorine for these purposes is 'bleaching powder,' which affords the gas when a little acid of any kind—vinegar, for example—is added to it (see Experiment 152).

Experiment 151.—Instead of dissolving Cl gas in water, pass it into *cold* solution of potassium hydrate (KOH)[1]—the *Liquor Potassæ* (B. P.) answers

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[1] If NH_4OH be substituted for KOH in the above experiment, a very different change occurs, for a quantity of *nitrogen* gas is obtained instead of a bleaching solution, thus—

$$4NH_4OH + 3Cl = N + 3NH_4Cl + 4H_2O.$$

well; when partially saturated with the gas, stop the current. The solution so obtained is colourless, and smells somewhat like ' bleaching lime.' A few drops of any acid added to a *portion* causes the evolution of chlorine, which is easily recognised by its colour and odour.

The action of Cl on KOH in the cold results in the production of a mixture of potassium chloride and *hypochlorite* in solution, thus—

$$2Cl + 2KOH = \underbrace{KCl}_{\substack{\text{Potassium} \\ \text{chloride.}}} + \underbrace{KOCl}_{\substack{\text{Potassium} \\ \text{hypochlorite.}}} + H_2O$$
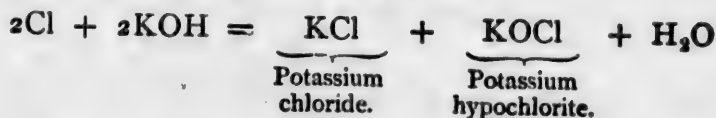
If into this liquid a piece of madder-dyed wool be stirred, the red colour is not destroyed, as the alkaline hypochlorite does not bleach, but, on the addition of a few drops of dilute hydrochloric or other acid, the colour is discharged. In this case the bleaching agent is chiefly chlorine, resulting from the following reaction—

$$KOCl + 2HCl = KCl + 2Cl + H_2O.$$
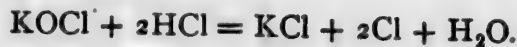
Potassium hypochlorite is therefore a convenient source of chlorine for bleaching, deodorising, and disinfecting purposes, but in all these cases acidulation is necessary in order to obtain the bleaching or deodorising effect.

The solution of *chlorinated soda* (B.P.) is obtained by passing Cl gas through solution of sodium car-

This is, in fact, a good method for the preparation of nitrogen gas, but the ammonia must always be present in excess, else there is risk of forming the dangerous chloride of nitrogen (see under Experiment 125).

bonate, when sodium hypochlorite and chloride are formed, and carbon dioxide gas is evolved—

$$Na_2CO_3 + 2Cl = NaCl + NaOCl + CO_2.$$
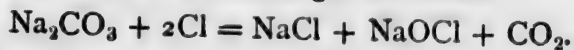
Experiment 152. — If we line the interior of a wide-mouthed bottle with moist slaked lime $(Ca''(OH)_2)$ and pass a slow current of Cl gas into the vessel, the gas is absorbed and combines with the lime, forming the ' bleaching lime ' or *chlorinated lime* of the B.P., commonly called ' chloride of lime '[1] :—

$$4Cl + \underbrace{3Ca''(OH)'_2}_{\substack{\text{Calcium} \\ \text{hydrate.}}} = \underbrace{CaCl_2}_{\substack{\text{Calcium} \\ \text{chloride.}}} + \underbrace{2Ca''OCl'OH'}_{\substack{\text{Calcium} \\ \text{chlorhydrate.}}} + 2H_2O$$
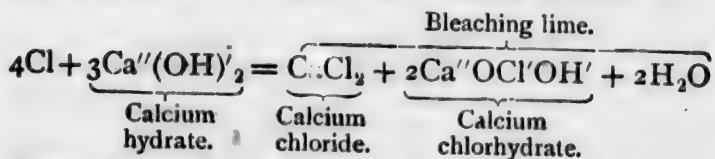
Bleaching lime.

On the large scale the slaked lime is spread in thin layers on shelves in large chambers to which Cl gas is admitted ; the latter is absorbed (just as in the bottle), and ' bleaching lime ' obtained as a dull white powder with a feeble odour like chlorine and only partially soluble in water, calcium hydrate separating and impurities in the lime used remaining undissolved.   The aqueous solution contains the two calcium salts above named. Bleaching powder or its solution affords HOCl and Cl gas on treatment with any acid (as in the case of KOCl), and is therefore a most convenient source of those bodies for bleaching or deodorising purposes.

The three bleaching salts above referred to are derived from the acid named *hypochlorous acid*, $H'O''Cl'$, which is best obtained by the action of

[1] Its empirical formula is $Ca_3Cl_2O_6H_6$, which requires 39 per cent of chlorine. The best samples rarely contain more than 38·5 per cent., and always contain more or less calcium chlorate.

its anhydride upon water. The anhydride is prepared by passing dry chlorine gas over dry mercuric oxide,[1] placed in a tube which is cooled. An orange yellow gas results from the action of the Cl on the oxide, and this is the anhydride Cl_2O, which can be easily liquefied by reducing the temperature to $-10°$ C.—

$$4Cl + 2HgO = \underbrace{Cl_2O}_{\substack{\text{Hypochlorous} \\ \text{anhydride.}}} + \underbrace{Hg_2Cl_2O}_{\substack{\text{Mercury} \\ \text{oxychloride.}}}$$
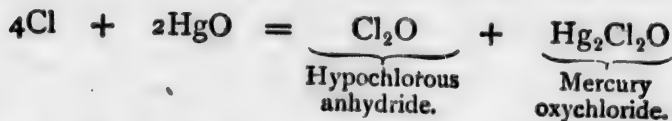
The gas is very explosive, the heat of the hand being often sufficient to decompose it into $2Cl$ and O ; it is therefore not a safe body for the junior student to prepare. 1 c.c. of water dissolves 20 c.cs. of the gas, and forms solution of hypochlorous acid—

$$Cl_2O + H_2O = 2HOCl$$

The solution is a powerful bleaching agent.

Experiment 153.—Instead of dissolving Cl gas in cold potassium hydrate, pass it into the boiling solution until gas ceases to be absorbed, and allow the liquid to cool. If the potash solution were originally strong, colourless crystalline plates will separate out even before the liquid is quite cold ; but if these crystals do not separate on cooling, evaporate the solution down to half its bulk and then cool , collect the crystals deposited on standing and throw them on a suitable filter ; pour a small quantity of cold water over them to wash away impurity, repeat the washing if necessary, and then dry. This body,

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[1] Prepared by precipitation. See Part III.

when pure, has a cool saline taste and is sparingly soluble in cold water, though easily dissolved with the aid of heat ; its name is *potassium chlorate* and its formula $KClO_3$ or $K'—O''—O''—O''—Cl'$, the body from which we have already prepared oxygen gas (see Experiment 57). In its preparation[1]—

$$6Cl + 6KOH = \underbrace{KClO_3}_{\substack{\text{Potassium} \\ \text{chlorate.}}} + \underbrace{5KCl}_{\substack{\text{Potassium} \\ \text{chloride.}}} + 3H_2O$$
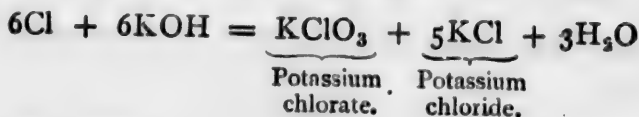
The KCl is a very soluble salt, and therefore remains in solution, while the slightly soluble chlorate crystallises out. When the latter is heated in a test-tube it melts and gives off oxygen, which can be easily recognised by its property of rekindling a match with a glowing tip. Here—

$$KClO_3 = KCl + 3O.$$
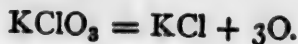
The white residue in the tube consists of potassium chloride, which is easily distinguished from the chlorate by its solution affording a white precipitate of silver chloride $(AgCl)$ when tested with silver nitrate. Potassium chlorate does not give a precipitate with

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[1] Instead of pure caustic potash, as above, the B. P. directs Cl gas to be passed through a mixture of solution of potassium carbonate (K_2CO_3) and slaked lime $(Ca(OH)_2)$. In this case—

$$12Cl + K_2CO_3 + 6Ca(OH)_2 = 2KClO_3 + CaCO_3 + 5CaCl_2 + 6H_2O.$$
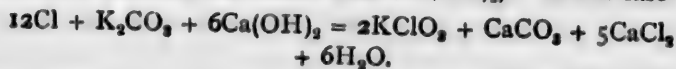
The mixture is afterwards boiled, then filtered from excess of slaked lime and the chalk $(CaCO_3)$ produced in the process, concentrated by evaporation, and the chlorate crystallised out from the solution.

silver nitrate, because silver *chlorate* is a very soluble salt.[1]

Experiment 154.—The ease with which the chlorate parts with its oxygen renders it a very powerful oxidising agent ; hence, if a few grains are mixed with a little powdered charcoal and heated on a knife blade, explosive combustion ensues.

Experiment 155.—Pour five or six drops of strong sulphuric acid into a test-tube and add a *very small* crystal of the chlorate, and gently warm ; the mixture becomes yellow, and a yellow gas is evolved which explodes very easily ; hence a loud crackling noise occurs on heating. The gas is a mixture of oxides of chlorine, which decompose into their constituents with explosive violence on gentle heating. This effect is very characteristic of a chlorate, but in applying the test direct the mouth of the tube away from the person.

Experiment 156.—Powder separately a gram or so of potassium chlorate and of dry loaf sugar ; mix the powders on paper with a glass rod, place the

---

[1] Free chloric acid ($HClO_3$) is obtained by adding to a saturated solution of potassium chlorate a strong solution of hydrofluosilicic acid (H_2SiF_6, see page 267) ; the potassium unites with the latter, forming the sparingly soluble salt K_2SiF_6, which is precipitated, while monobasic chloric acid remains in solution—

$$2KClO_3 + H_2SiF_6 = 2HClO_3 + K_2SiF_6.$$

No anhydride of this acid is yet known. We are acquainted with another body, chlorous acid ($HClO_2$), which is intermediate between hypochlorous and chloric acids, but, like the latter, it is not as yet of any practical importance. The anhydride Cl_2O_3 is known.

mixture on a metal plate and touch the powder with a rod dipped in oil of vitriol; violent combustion ensues, the sugar (a compound of carbon, hydrogen, and oxygen) burning in the available oxygen of the chlorate.

Experiment 157.—Dissolve some of the chlorate in water, add a few drops of indigo solution, and then some strong sulphuric acid. Note that the blue colour is destroyed ; as might be anticipated, this bleaching action is due to oxidation.

Experiment 158.—Again heat some potassium chlorate in a tube of hard glass. The salt fuses as before, and oxygen is given off ; but, if the heat be steady throughout and not very strong, the contents of the tube become solid, and the evolution of gas ceases. On raising the temperature still higher, gas is again evolved, and in larger quantity than before.

The check just observed occurs when only one-third of the total oxygen has been driven off as gas, and the residue is found to consist of two salts, potassium chloride and potassium perchlorate—a body which is very slightly soluble in cold water, and which is therefore left behind to a great extent when the cooled mass is digested with cold water. The following equation represents the change—

$$2KClO_3 \;=\; \underbrace{KCl}_{\substack{\text{Potassium}\\\text{chloride.}}} \;+\; \underbrace{KClO_4}_{\substack{\text{Potassium}\\\text{perchlorate.}}} \;+\; 2O$$
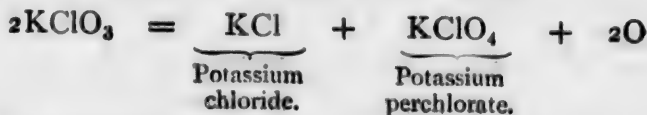
The perchlorate is much less easily decomposed than the chlorate, but ultimately yields up all its oxygen like the chlorate. Hence, in preparing oxy-

gen gas from potassium chlorate, the decomposition takes place in two stages, though we commonly express the change by means of a single equation.

When potassium perchlorate is heated with strong sulphuric acid, an acid distillate is obtained which Roscoe found to contain perchloric acid, $HClO_4$— one of the most powerful oxidising agents known, as mere contact with it suffices to kindle paper or wood.[1] No anhydride corresponding to perchloric acid has been obtained.

Neither the acid nor its potassium salts are as yet of any practical importance, but much interest attaches to the former as the highest term of the following series of chlorine acids—

		Acids.	Anhydrides.
Hydrochloric acid	.	HCl	—
Hypochlorous acid	.	$HClO$	Cl_2O
Chlorous acid	. .	$HClO_2$	Cl_2O_3
Chloric acid	. .	$H\dot{C}lO_3$	Cl_2O_5 (?)
Perchloric acid	. .	$HClO_4$	Cl_2O_7 (?)

All these acids contain but one atom of hydrogen within the molecule replaceable by a metal, and are therefore monobasic. They may be regarded as successive oxides of hydrochloric acid (HCl), and their formulæ will be most easily remembered when they are thus viewed. Moreover, the series of bodies may be cited as remarkable illustrations of the *Law of Multiple Proportions.*

[1] The perchlorate does not bleach indigo in presence of sulphuric acid, and is thus easily distinguished from the chlorate.

CHAPTER XVI.

EXPERIMENTS WITH IODINE.

Experiment 159.—Dissolve in water, in a test-tube, a few crystals of the salt potassium iodide (KI), and add a few drops of chlorine water to the liquid. Note that a brown-red colour is immediately produced, and black, heavy particles separate from the liquid if the solutions are strong and sufficient chlorine is added. When the particles have subsided, pour off the coloured liquid, and drain it away as completely as possible from the deposit. Now, without drying, apply a gentle heat to the black substance ; a *violet-coloured* vapour is produced, which condenses on the cool upper part of the tube in black, shining metallic-looking scales, the water present volatilising and condensing at the same time. This metal-like substance (or 'metalloid'), characterised by its easy volatility and beautifully coloured vapour, is an element, and is called

$$\text{IODINE}\text{---}I' = 127.$$

The compound with potassium used in this experiment is easily decomposed by chlorine, as we have seen ; the latter seizes the metal and forms potassium chloride, while iodine is displaced, thus—

$$K'I' + Cl' = K'Cl' + I'.$$

Experiment 160.—Potassium iodide and chloride are obviously analogous bodies ; hence the method already used for the separation of chlorine from its metallic compounds (Experiment 137) might serve for the separation of iodine from the metallic iodide. Mix the latter, or its solution, with some manganese peroxide (MnO_2) in a test-tube, add a few drops of strong sulphuric acid, and apply heat. Violet vapours of iodine are given off, and condense on the sides of the tube as before ; the by-products manganese and potassium sulphates are left—

$$2KI + MnO_2 + 2H_2SO_4 = 2I + MnSO_4 + K_2SO_4 + 2H_2O.$$
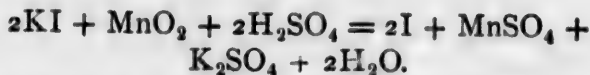
The reaction is therefore precisely analogous to that in which chlorine is evolved by the action of MnO_2 and H_2SO_4 on common salt.

Iodine is widely distributed throughout nature, but in small quantities, and always in combination, though chiefly with potassium, sodium, or magnesium, and sometimes, though rarely, with silver. It is present in many mineral waters, and in sea water ;[1] from the latter the iodides are extracted by various sea-weeds, and these, when collected, partially dried, and burned, afford an ash which is termed 'kelp,' and from this ash much of the iodine of commerce is extracted. The process of extraction consists in digesting the kelp with water, which dissolves out a considerable number of soluble salts, including the iodides (and bromides, see page 250) ; the solution

[1] It is also present in small quantity in 'Chili nitre '—sodium nitrate—in cod-liver oil, sponge, &c.

is filtered, evaporated, and the less soluble salts crystallised out and thus separated from the very soluble iodides. The remaining liquor is treated with strong sulphuric acid, and some sulphur is then separated and removed. The acid liquid is next poured into large stills or retorts, manganese dioxide added, and heat applied. Iodine is separated from the iodide as in the above experiment, and distils over;

Fig. 81.
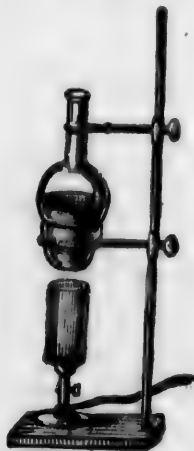
it is condensed in a number of tubular receivers, from which it is removed, and, when sufficiently dry, is sent into commerce in a somewhat crude condition. Free iodine and some of its compounds are largely employed in medicine, but it is desirable that the crude element should be purified before it is so used.

Experiment 161.—Place a few grams of crude iodine in a crucible, which is to be covered as shown (fig. 81) with a flask containing cold water. A gentle heat is applied to the crucible, and after a few minutes the flask is removed; then the small quantity of iodine deposited upon it, with a few whitish needle-shaped crystals of 'iodide of cyanogen,' which usually accompany it, must be scraped off; the flask is replaced and gentle heat again applied. After some time large crystalline plates of pure iodine will be found attached to the bottom of the flask; these are to be removed and preserved. If the iodine used in the first instance

were pure, no residue should be left in the crucible at the end of the operation. This process is one of *sublimation*—in which a solid is deposited from a state of vapour.

The specific gravity of pure solid iodine is 4·95 (water = 1).

The element gives off vapour at ordinary temperatures, and it becomes a liquid when heated to 114° C.; it boils at 200° C., and affords its magnificently coloured vapour in abundance, as we have already seen. The specific gravity of the vapour is 125·9, but the atomic weight is slightly higher, or 127.

Experiment 162.—Add to some water in a test tube a few fragments of solid iodine; shake, and allow to stand for some time. The water gradually acquires a brownish-yellow tint, but the proportion ultimately dissolved is very small, as careful experiments have shown that iodine requires nearly 6,000 times its weight of water at mean temperature for solution.

Experiment 163.—Add some litmus to a portion of the dissolved iodine; little or no bleaching is observed, unlike the rapid decoloration that takes place with chlorine.

Experiment 164.—Rub a few pieces of common starch with water in a mortar, and pour the mixture into a capsule. Heat nearly to boiling, with constant stirring, and when the mixture thickens and becomes gelatinous remove the source of heat. Stir the 'made starch' up with warm water until a thin 'mucilage' is obtained, and preserve this for use. Add a few drops of the mucilage to half a test-tube full of

aqueous solution of iodine, and shake ; a beautiful *blue* liquid is obtained, owing to the formation of an ill-defined compound of starch and iodine. This is an excellent and most characteristic test for the free element. Heat the contents of the test tube nearly to boiling, note that the colour *disappears*, but, on cooling, it reappears. Therefore the starch test should always be applied in *cold liquids*.

Experiment 165.—Add a drop or two of starch mucilage to a solution of potassium iodide.[1] No change whatever is observed ; therefore iodine in chemical combination does net give the reaction. Now add to the mixture a drop of chlorine water, or of strong brownish-coloured nitric acid ; iodine is instantly set free and the blue compound formed.

Experiment 166.—Again, put some pieces of iodine into a test-tube with some water ; we already know that very little dissolves, even on long standing ; but now throw in a few crystals of potassium iodide, and observe that on agitating the liquid it becomes of a deep reddish-brown colour, and the solid iodine disappears as the potassium iodide dissolves. The element is therefore much more soluble in potassium iodide solution than in plain water. In this case solution is probably due to the formation of a potassium tri-iodide of the formula KI,I_2.

Advantage is taken of this fact in the preparation of the liquor and tincture of iodine of the British Pharmacopœia. In the latter case, however, rectified spirit of wine is the solvent, the solubility of iodine

[1] A very dilute solution.

in alcohol also being increased by the presence of potassium iodide.

Experiment 167.—Add a few drops of *chloroform* to a simple aqueous solution of iodine, and shake. The chloroform subsides on standing, and has a fine purplish colour, as it carries with it the iodine, which is very soluble in it, and is thus easily removed from the water. Iodine is also soluble with ease in ether and in carbon disulphide.

Fig. 82.

Iodine does not burn in, neither does it directly combine with, free oxygen ; but it readily unites with many metals and non-metals.

Experiment 168.—Rub a fragment of iodine with some mercury in a mortar ; a reddish powder is first produced, which becomes green if a little more mercury be added and the trituration be continued for a sufficient time.[1] The resulting compound is 'green iodide of mercury' —$Hg''_2I'_2$—thus formed by direct union of the elements.

Experiment 169.—Take a large and wide test-tube—about 10 c.cs. long by 3 c.cs. diameter; introduce a few fragments of iodine, and support the tube in a convenient holder. Apply heat to the tube so as to convert the iodine into vapour, and when the latter half fills the

[1] The addition of a few drops of alcohol hastens the process by dissolving some of the iodine and thus facilitating chemical action, as in Experiment 6, Part I.

tube plunge into the vapour a very *small* piece of dry phosphorus contained in the deflagrating spoon (fig. 82). The phosphorus takes fire in the iodine

FIG. 83.

vapour and burns for some time; if the phosphorus be in excess, the colour of the iodine vapour disappears, owing to complete combination of the latter with the phosphorus, an iodide of the latter body being formed—thus, $P + 3I = PI_3$. If, when the tube and its contents have cooled down, a few drops of cold water are allowed to fall upon the dark-coloured body left in the tube, a fuming gas that reddens blue litmus-paper will be given off; this gas proves on examination to be a compound analogous to hydrochloric acid, and is termed hydriodic acid—HI—the only known compound of the two elements. We shall now repeat the experiment in such a way as to afford a considerable supply of this gas.

HYDRIODIC ACID = HI. 1 *Vol weighs* 63·76 *c.grs.*
Molecular weight = 128.

Experiment 170.—Fit up a flask as shown, fig. 83. Remove the cork and tubes and introduce into it two grams of red or '*amorphous*' phosphorus--not the ordinary waxy variety, as its use in quantity is attended with danger—and 15 grams of powdered

iodine. A very little heat serves to determine the union of the two bodies, and a nearly black mass, consisting chiefly of phosphorus tri-iodide, is formed, as in the last experiment. Insert the cork and support the flask as shown ; then close the stopcock of the funnel and half fill the latter with water. Now turn the stopcock so as to allow the water to fall drop by drop on the iodide in the flask. As each drop of water falls, a colourless and heavy gas is evolved which can be easily collected by passing the straight portion of the delivery-tube into a dry jar ; the air is displaced and a jar full of the dense gas obtained. In this way several jars are to be filled and then covered with glass plates. The hydriodic acid gas thus obtained results from the following reaction—

$$\underset{\substack{\text{Phosphorus}\\\text{tri-iodide.}}}{PI_3} \quad + \quad 3H_2O \quad = \quad \underset{\substack{\text{Hydriodic}\\\text{acid.}}}{3HI} \quad + \quad \underset{\substack{\text{Phosphorous}\\\text{acid.}}}{H_3PO_3}$$
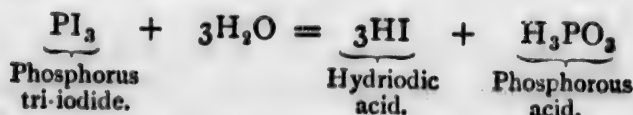
The phosphorous acid remains behind in the flask. When sufficient gas has been obtained, stop the evolution by turning the stopcock so as to prevent the entrance of more water until a further supply of gas is required. Now turn to the jars of gas.

Experiment 171.—Note that it is colourless, but on removing the plate from a jar it fumes in air ; it has an irritating smell and acid reaction to litmus-paper. Pour some chlorine gas from a tube in which it is generated (by the action of an acid on a little bleaching powder) into the bottle of hydriodic acid gas. Instantly the beautiful violet vapour of free

iodine appears, thus proving the presence of that element in the gas.   In this reaction—

$$Cl + HI = HCl + I.$$

Experiment 172.—Take a large beaker or a tumbler and drop a little strong and brown-coloured nitric acid into it.   Then pour from a considerable height hydriodic acid gas from a jar into the tumbler, and note that free iodine quickly appears in the latter. We thus prove that the gas is decomposed by the powerful oxidising agent nitric acid, iodine being liberated ; and we also prove that hydriodic acid is a very heavy gas, since it can be easily poured, like a liquid, through air.   Its specific gravity is 63·76 ($H = 1$), 1 *vol* weighing 63·76 c.grs.   Its molecular weight is $63·76 \times 2 = 127·52$, and its formula HI. It is nearly 4·5 times heavier than air.

Experiment 173.—Remove the plate from another jar and immediately bring its mouth under the surface of some water.   The latter rapidly rises, proving that HI is very soluble in water.

Experiment 174.—A strong solution of HI gas in water is used in medicine to a small extent, and it is easily prepared in the following way.   Take a clean jar, introduce some water into it, and allow the delivery tube of the flask (fig. 83) to approach the surface of the water, but *not* to touch the latter.   On allowing water to fall slowly from the funnel on the remaining phosphorus tri-iodide, more heavy hydriodic acid gas is evolved, which then falls on the surface of the water and is at once absorbed.   If the delivery tube dipped under the surface of the water, absorption

would take place so rapidly that the solution would rush back into the flask. A liquid can be obtained containing 57 per cent. of hydriodic acid, whose specific gravity is 1·9, or almost double that of water. The aqueous solution and the gas are easily decomposed when exposed to air and light, iodine being liberated and water formed—

$$2HI + O = H_2O + 2I.$$
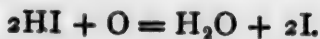
The iodine is not deposited from the aqueous acid unless decomposition has proceeded very far, but is dissolved by the acid, in which the element is very freely soluble.

Experiment 175.—Pour into a capsule some of the dilute solution of hydriodic acid prepared in the last experiment, and just neutralise with solution of caustic potash ; then evaporate the solution until a crust begins to form on the surface of the liquid, and allow to cool. Small cubic crystals separate out which are identical with the *potassium iodide* employed in Experiment 159. The following change takes place on neutralising the hydriodic acid with the alkali—

$$HI + KOH = KI + H_2O.$$
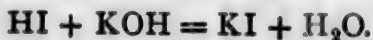
This is the easiest mode of preparing potassium iodide and many other iodides (i.e., by saturating the acid with the hydrate, oxide, or the carbonate of the metal or other basic radicle), but much of the commercial potassium iodide is prepared by the method employed in Experiment 181.

We have already seen that potassium iodide and chloride are analogous bodies, and can afford the

non-metallic radicle by similar treatment. Now we know from Experiments 126, 127 that a chloride affords hydrochloric acid when treated with oil of vitriol ; we have therefore to ascertain whether or not an iodide will afford *hydriodic acid* by similar treatment.

Experiment 176.—Add a few crystals of potassium iodide to a small quantity of strong sulphuric acid contained in a test-tube, and warm. Instead of the colourless hydriodic acid gas we should expect to see evolved, violet vapours of iodine are given off, while a yellow body that can be identified as sulphur separates in the tube, and a suffocating smell is perceived (sulphur dioxide), or an odour of rotten eggs is developed (sulphuretted hydrogen). The sulphur and its compounds separated in this reaction are all products of *deoxidation* of sulphuric acid, and the most probable cause of this is hydriodic acid, which, as we already know, parts easily with its hydrogen, and the latter then available forms water with more or less of the oxygen of the sulphuric acid, and iodine is set free. Hence, though hydriodic acid is doubtless formed according to the equation

$$KI + H_2SO_4 = HI + KHSO_4,$$

it is immediately destroyed in the way just indicated ; but the detailed examination of the reaction must be reserved until we study oil of vitriol.

If this view be correct, we ought to get hydriodic acid gas alone on heating the iodide with a strong acid not so readily reduced or deoxidised as sulphuric acid.

Experiment 177.—Heat a few crystals of the potassium iodide as before, with syrupy *phosphoric*

acid,[1] and note that hydriodic gas is evolved and little if any iodine is separated.

Experiment 178.—Add a few drops of silver nitrate to a solution of potassium iodide, and note that a pale yellow precipitate of silver iodide is formed—

$$AgNO_3 + KI = AgI + KNO_3.$$

The precipitate is insoluble in dilute nitric acid, and is very slightly soluble in ammonia solution.

Experiment 179.—Add to some dissolved potassium iodide a few drops of lead nitrate solution. Note that a fine bright *yellow* precipitate of lead iodide is at once obtained—

$$2K'I' + Pb'' (NO_3)'_2 = Pb''I_2 + 2KNO_3.$$
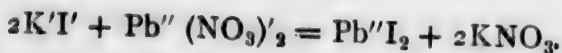
This precipitate is somewhat soluble in boiling water, and separates out on cooling in fine golden spangles.

Experiment 180.—To another portion of the iodide solution add mercuric chloride ($Hg''Cl_2$) or 'corrosive sublimate.' By the addition of the first drop, a precipitate, varying in tint from salmon colour to bright scarlet, is obtained, but this dissolves on shaking the liquid. On continuing the addition of the mercury solution, a point is reached at which a scarlet precipitate is obtained which does not dissolve on agitation ; this is scarlet mercuric iodide—

$$Hg''Cl_2 + 2K'I' = HgI_2 + 2KCl.$$
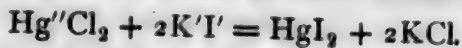
This scarlet iodide is easily soluble in excess of potassium iodide, producing a colourless solution, as we have seen ; the latter contains a soluble and colourless double iodide of mercury and potassium, HgI_2, $2KI$.

[1] See PHOSPHORUS.

A strongly alkaline solution of this double iodide constitutes *Nessler's test*[1] for ammonia (see page 21).

Hydriodic acid and iodides are thus easily distinguished by the reactions we have learned in the course of these experiments.

Experiment 181. — Warm some caustic potash solution in a test-tube, and add iodine, in small portions at a time, until the liquid assumes a permanent yellowish colour. The element dissolves and forms two salts—one potassium *iodide*, KI, the other potassium *iodate*, KIO_3, thus—

$$6I + 6KOH = 5KI + KIO_3 + 3H_2O.$$

This reaction is precisely similar to that which occurs when chlorine acts on a hot and strong solution of caustic potash, as in Experiment 153, but the iodate cannot be separated from the iodide[2] quite as easily as can the chlorate from the chloride.

Pour the solution into a small porcelain dish and evaporate to complete dryness. Remove a small portion of the dry residue, which is a mixture of the

[1] *Nessler's test solution* is thus made—Dissolve 5 grams of potassium iodide in a very small quantity of hot water; add to the liquid a saturated solution of mercuric chloride until the red iodide just ceases to redissolve. Now add 12 grams of caustic potash, previously dissolved in a little water; mix and make up the total volume to 100 cubic centimeters with distilled water; finally add a few drops more of the mercuric chloride solution, allow to stand, and draw off the clear liquid for use; but it must not be filtered through paper. For the action of the test see under MERCURY SALTS, Part III. p. 104.

[2] The separation is best effected by evaporating the solution to complete dryness and digesting the residue with strong alcohol, which dissolves the iodide but not the iodate.

two iodine salts; dissolve in some water in a test-tube, add a drop of starch mucilage and then some dilute acetic acid. Note that a blue colour is quickly developed after the addition of the acid, proving that iodine has been set free. In this case the acetic acid displaces hydriodic acid from the iodide, and iodic acid from the iodate, and the two acids thus liberated at once react, producing free iodine and water, thus—

$$HIO_3 + 5HI = 6I + 3 H_2O.$$
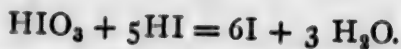
Now return to the dry residue of evaporation; powder it in the dish and mix with one-fourth its bulk of powdered charcoal. Heat the mixture until it is seen to melt, before which it glows for a short time, owing to the combustion of the charcoal or carbon in the oxygen of the iodate, carbon dioxide gas being formed and evolved, while the iodate is reduced to potassium iodide—

$$2KIO_3 + 3C = 2KI + 3CO_2.$$
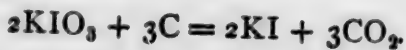
Then allow the mass to cool, add some hot water, and filter from residual charcoal. The solution now contains only potassium iodide (which can be crystallised out), for on adding starch and acetic acid no blue colour is produced.

Most of the potassium iodide of commerce is prepared by the process just followed, and samples of the iodide can be tested for iodate by the method indicated.

Potassium iodate is sometimes used as a test for sulphurous acid (see that body) in acetic and other acids; the iodate used for this purpose may be separated from

iodide as stated, or, better still, may be specially prepared by the following instructive method directed in the British Pharmacopœia.

Experiment 182.—Heat together in a flask two or three grams of powdered iodine with an equal weight of potassium chlorate and about 10 c.cs. of water acidulated with 5 or 6 drops of strong nitric acid. Chlorine gas is evolved, and the mixture is digested until the colour of the iodine grad̶ ̶ disappears ; then boil for a minute or two ̶ ̶ liquid out into a capsule, and evaporate to dryness at a gentle heat. The residue consists wholly of potassium iodate, the chlorine and the nitric acid having almost completely disappeared.

This amounts to a replacement of chlorine in potassium chlorate by iodine, thus—

$$KClO_3 + I = KIO_3 + Cl.$$
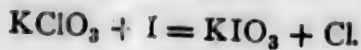
The small amount of nitric acid used facilitates this replacement by liberating small successive quantities of chloric acid, which latter is directly acted upon by iodine.

This decomposition is remarkable, because it proves that chlorine is displaced by iodine from its *oxidised* compound the chlorate, whereas we already know that chlorine easily displaces iodine from the *unoxidised* compound KI. The order of 'affinity' of chlorine and iodine is therefore here determined by the presence or absence of oxygen, and this is found to be generally true.

Iodine is converted into iodic acid when boiled in a flask with strong nitric acid, and colourless

crystals of HIO_3 are obtained on evaporation. When these crystals are heated for some time to 170° C. they are decomposed into water and iodine pentoxide (I_2O_5) or iodic anhydride, thus—

$$2HIO_3 = I'_2O_5'' + H_2O.$$
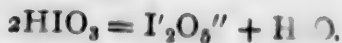
The anhydride, when further heated to the temperature of boiling olive oil, is resolved into iodine and oxygen.

Although the formula of iodic anhydride is precisely similar to that of nitric anhydride ($N^v_2O''_5$), it is not necessary to assume that iodine is a five-link or pentad element like nitrogen, or that it is more than a monad or uni-link body, as the constitution of the iodic anhydride and acid can be thus explained on the latter supposition—

Oxide, $I'—O''—O''—O'—O''—O''—I'$.
Acid, $H'—O''—O''—O''—I'$.
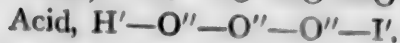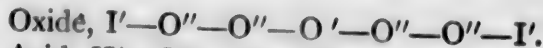
The salts of a still higher acid are known, viz. periodic acid—HIO_4—the analogue of perchloric acid.